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HETEROCYCLIC COMPOUNDS

Part XV. Coumarins from Pyrogallol Derivatives

By R. D. Desai and C. K. Mavani
(From the Department of Chemistry, St. Xavier's College, Bombay)

Received July 12, 1941

Though a considerable amount of work has recently been done on the condensation of resorcinol derivatives with β-ketonic esters in the presence of various condensing agents, practically no work on similar lines exists with regard to the pyrogallol derivatives. Desai and Ekhlas[1] have observed that whereas pyrogallol undergoes the coumarin condensation with great facility gallacetophenone condenses with aceto-acetic ester in the presence of phosphoryl chloride giving 4-methyl-6-acetyl-7 : 8-dihydroxy coumarin in small amount. We, therefore, thought it interesting to extend this observation to other pyrogallol derivatives, containing different substituents. With this object in view, we have condensed gallic acid as well as its methyl and ethyl esters, pyrogallol carboxylic acid as well as its methyl and ethyl esters, and 4-ethyl-pyrogallol with aceto-acetic and benzoyl acetic esters with the results described hereunder.

Gallic acid as well as its methyl and ethyl esters and pyrogallol carboxylic acid did not undergo the coumarin condensation with aceto-acetic and benzoyl-acetic esters under the influence of any condensing agent, while methyl as well as ethyl pyrogallol carboxylate and 4-ethyl-pyrogallol condensed smoothly with these ketonic esters in the presence of 73 per cent. sulphuric acid.

These results show that the effect of the substituents like acetyl, carboxyl, carbomethoxy, or carboethoxy, and ethyl groups is to reduce the reactivity of pyrogallol so far as the coumarin condensation is concerned. However, there is a great difference when the effect of these groups is considered quantitatively, and this can be arranged in the order of carboxyl > acetyl > carbomethoxy > ethyl. Moreover, as β-resorcylic acid gives coumarins in the presence of sulphuric acid in contrast with pyrogallol carboxylic acid, the conclusion is unavoidable that the resorcinol derivative is more reactive than that of pyrogallol. Further, the non-reactivity of methyl gallate and the reactivity of methyl pyrogallol carboxylate show that the inhibitory effect exerted by these groups is partly polar and partly steric.

Having observed the reactivity of ethyl-pyrogallol carboxylate and 4-ethyl-pyrogallol with aceto-acetic ester, the condensation of these two phenols with α-methyl-, α-ethyl- and α-propylacetoacetic esters was studied, and it was found that although the reaction did take place, the yield of coumarins was small, and went on decreasing as the size of the alkyl groups went on increasing.

Before concluding, we wish to record the fact that in contrast with 7-hydroxy- and 5-hydroxy coumarin derivatives, the acetyl derivatives of which undergo the Fries migration of acyl groups, the 7 : 8-dihydroxy- as well as 6-hydroxy-coumarin derivatives do not respond to this reaction. The same also holds good in the case of 6-hydroxy- and 7 : 8-dihydroxy-chromones and flavones.

Experimental

Preparation of Pyrogallol Carboxylic Acid.—The following improved process was found to give the best yield of the pure acid. A solution of pyrogallol (20 g.), anhydrous sodium bicarbonate (20 g.) and sodium sulphate (5 g.) in water (50 c.c.) was heated on water-bath under reflux for 4 hours. The cooled solution was poured into an excess of ice-cold concentrated hydrochloric acid and the solid that separated out was filtered off. The acid crystallised from hot water in long, stout needles, m.p. 215° (yield = 50 per cent.). Its aqueous solution gave violet colouration with alcoholic ferric chloride. Attempts to condense it with aceto-acetic ester under all conditions proved abortive.

Condensation of Methyl Pyrogallate with Aceto-acetic Ester and Formation of 4-Methyl-6-carbomethoxy-7 : 8-dihydroxy Coumarin.—A solution of methyl pyrogallate (4 g.) and aceto-acetic ester in 73 per cent. sulphuric acid (30 c.c.) was poured over ice after 36 hours. The solid crystallised from alcohol in colourless needles, m.p. 209° (yield = 30 per cent.). It dissolved readily in hydroxylic solvents, sparingly in benzene and was almost insoluble in petroleum ether. Its yellow alkaline solution was non-fluorescent, and the alcoholic solution gave green colouration with alcoholic ferric-chloride. [Found: C, 57·3; H, 4·1; $C_{12}H_{10}O_6$ requires C, 57·6; H, 4·0 per cent.]

4-Methyl-6-carboethoxy-7 : 8-dihydroxy Coumarin was similarly obtained from ethyl-pyrogallate (yield = 25 per cent.). It crystallised from alcohol in colourless needles, m.p. 211°, and had the properties of its methyl analogue. [Found: C, 58·9; H, 4·8; $C_{13}H_{12}O_6$ requires C, 59·1; H, 4·6 per cent.]

3 : 4-Dimethyl-6-carboethoxy-7 : 8-dihydroxy Coumarin obtained from α-methylacetoacetate and ethyl-pyrogallate crystallised from alocohol in

asbestos-like needles, m.p. 230°. Its alcoholic solution gave green colouration with alcoholic ferric chloride (yield = 10 per cent.). [Found: C, 60·2; H, 5·3; $C_{14}H_{14}O_6$ requires C, 60·4; H, 5·1 per cent.]

3-*Ethyl*-4-*methyl*-6-*carboethoxy*-7: 8-*dihydroxy Coumarin* prepared from ethyl-pyrogallate and α-ethylacetoacetate crystallised from alcohol in needles, m.p. 209–10° (yield = 8 per cent.). [Found: C, 61·4; H, 5·7; $C_{15}H_{16}O_2$ requires C, 61·6; H, 5·6 per cent.]

3-*Propyl*-4-*methyl*-6-*carbomethoxy*-7: 8-*dihydroxy Coumarin* obtained from α-propylacetoacetate and ethyl pyrogallate crystallised from alcohol in colourless needles, m.p. 203–04° (yield = 6–8 per cent.). [Found: C, 62·6; H, 6·1; $C_{16}H_{18}O_6$ requires C, 62·7; H, 5·9 per cent.]

4-*Phenyl*-6-*carboethoxy*-7: 8-*dihydroxy Coumarin* obtained from benzoyl-acetic ester and ethyl pyrogallate crystallised from alcohol in colourless needles, m.p. 217° (yield = 6 per cent.). [Found: C, 66·0; H, 4·5; $C_{18}H_{14}O$ requires C, 66·3; H, 4·3 per cent.]

Condensation of 4-*Ethylpyrogallol with β-Ketonic esters*: 4-*Ethylpyrogallol* was prepared by the Clemmensen Reduction of gallacetophenone which was prepared by the Fries Transformation of pyrogallol triacetate.

An intimate mixture of anhydrous aluminium chloride (24 g.) and pyrogallol triacetate (12 g.) was slowly heated in an oil-bath till the fumes began to appear. The temperature was maintained at 130–40° for one hour, the contents cooled, and treated with ice-cold hydrochloric acid. As no solid appeared, the solution was extracted with ether after being saturated with sodium chloride, and the solid recovered from the dried ethereal solution. Yellowish-red crystals of gallacetophenone were obtained. It crystallised from ligroin in yellowish needles, m.p. 168° (yield = 65–70 per cent.). In our opinion this method is easier than most of those described in literature.[2]

Clemmensen Reduction of Gallacetophenone to 4-*Ethylpyrogallol.*—A mixture of the ketone (5 g.), amalgamated zinc (20 g.) and hydrochloric acid (100 c.c.), was heated on sand-bath for 5 hours, cooled, and the contents extracted with ether. The dried, ethereal solution gave 4-ethyl-pyrogallol which crystallised from benzene in colourless needles, m.p. 106°, as described by Erdtmann.[3]

4-*Methyl*-6-*ethyl*-7: 8-*dihydroxy Coumarin* obtained from 4-ethyl-pyrogallol and aceto-acetic ester crystallised from alcohol in colourless, lustrous needles, m.p. 205° (yield = 70 per cent.). [Found: C, 65·3; H, 5·6; $C_{12}H_{12}O_4$ requires C, 65·4; H, 5·5 per cent.]

The coumarin is soluble in alcohol, acetic acid, acetone, moderately so in benzene, but insoluble in petrol. Its alkaline solution is orange and nonfluorescent.

The diacetyl derivative crystallised from alcohol in white needles, m.p. 174°. [Found: C, 62·9; H, 5·5; $C_{16}H_{16}O_6$ requires C, 63·1; H, 5·3 per cent.]

When heated in contact with anhydrous aluminium chloride (Fries Migration), the original dihydroxy-coumarin, m.p. 205°, was obtained. It did not undergo nitration under any conditions.

3: 4-*Dimethyl*-6-*ethyl*-7: 8-*dihydroxy Coumarin* prepared from α-methyl-acetoacetic ester and 4-ethyl-pyrogallol crystallisd from alcohol in colourless needles, m.p. 244° (yield 50 = per cent.). [Found: C, 66·5; H, 6·2; $C_{13}H_{14}O_4$ requires C, 66·6; H, 6·0 per cent.]

The diacetyl derivative crystallised from alcohol in lustrous needles, m.p. 187°. It could not be nitrated, neither did it undergo the Fries Migration. [Found: C, 63·9; H, 5·9; $C_{17}H_{18}O_6$ requires C, 64·1; H, 5·7 per cent.]

3: 6-*Diethyl*-4-*methyl*-7: 8-*dihydroxy Coumarin* obtained from α-ethyl-aceto-acetate and 4-ethyl-pyrogallol crystallised from alcohol in white, lustrous needles, m.p. 202°, and shared the usual properties of its analogues (yield = 30 per cent.). [Found: C, 67·5; H, 6·7; $C_{14}H_{16}O_4$ requires C, 67·7; H, 6·5 per cent.]

The Diacetyl derivative crystallised from alcohol in needles, m.p. 167°. [Found: C, 64·8; H, 6·3; $C_{18}H_{20}O_6$ requires C, 65·0; H, 6·1 per cent.]

3-*Propyl*-4-*methyl*-6-*ethyl*-7: 8-*dihydroxy Coumarin* prepared from α-propyl aceto-acetic ester and 4-ethyl-pyrogallol crystallised from alcohol in needles, m.p. 159° (yield = 25 per cent.). [Found: C, 68·5; H, 7·0; $C_{15}H_{18}O_4$ requires C, 68·7; H, 6·9 per cent.]

The diacetyl derivative crystallised from alcohol in needles, m.p. 147°. [Found: C, 65·6; H, 6·6; $C_{19}H_{22}O_6$ requires C, 65·9; H, 6·4 per cent.]

4-*Phenyl*-6-*ethyl*-7: 8-*dihydroxy Coumarin* prepared from benzoylacetic ester and 4-ethyl-pyrogallol crystallised from alcohol in colourless straw-like needles, m.p. 145° (yield = 70 per cent.). [Found: C, 72·2; H, 5·2; $C_{17}H_{14}O_4$ requires C, 72·3; H, 5·0 per cent.]

The diacetyl derivative crystallised from alcohol in white, silky needles, m.p. 120°. It undergoes neither nitration nor Fries Migration. [Found: C, 68·6; H, 5·0; $C_{21}H_{18}O_6$ requires C, 68·8; H, 4·9 per cent.]

We take this opportunity of expressing our cordial thanks to Rev. Father A. M. Coyne, S.J., Principal of the College, and (*late*) Prof. R. N. Bhagwat, the Director of the Laboratories, for their kind interest in this work.

Summary

The condensation of gallic acid, pyrogallol carboxylic acid as well as their methyl and ethyl esters, gallacetophenone and 4-ethyl-pyrogallol with aceto-acetic ester, shows that all these groups exercise inhibitory effect in the Pechmann reaction to a varying extent. As β-resorcylic acid is reactive in such cases, it follows that the derivatives of pyrogallol are less reactive than those of resorcinol. The diacetyl derivatives of 7: 8-dihydroxy-coumarins do not undergo the Fries Migration.

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THE CONDENSATION OF ALDEHYDES WITH AMIDES

Part IX. The Condensation of *o*-Nitrobenzaldehyde

By P. I. Ittyerah and Kantilal C. Pandya
(*Chemistry Laboratory, St. John's College, Agra*)

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In Part VII of this series (Pandya and Varghese[1]), it has been pointed out that the aldehyde-amide condensations have three interesting features, *viz.*, (i) the influence of a trace of pyridine, (ii) the nature of the condensation-product and (iii) the yield. These seem to be vitally related to the group that happens to be present on the ring of the aromatic aldheyde: as for example, the influence of the free hydroxy, or phenolic, group appears to be very different from that of the methoxy and the methylene-dioxy groups. It may be added that cinnamaldehyde also seems to fall in with the latter class (Mehra and Pandya[2]). In order to find out whether a distinct group like the nitro has any modifying influence, a comparison has also been made (in Part VIII, Pandya and Varghese[3]) of the condensations of the same eight amides with piperonal and with 6-nitropiperonal. In respect of (i) and (ii) above, there was little difference, but in respect of (iii) as well as of the speed of the reaction, the difference was noticeable. It is also clear that different amides also make a great difference among themselves, and this, therefore, may be put down as another important factor governing the reaction as well as the final yield. In fact, peculiar results have been obtained with formamide and have been referred to already.

In order to judge the real influence of the nitro group, it is necessary to select nitrobenzaldehydes, where there are no other interfering groups (as in 6-nitropiperonal) and where also there is only one single nitro group. The results of this study are presented in this and the succeeding paper.

The aldehyde-amide condensation, under different conditions, has been very extensively studied, and of *o*-nitrobenzaldehyde itself condensations with three different amides, formamide, acetamide and benzamide, are mentioned in the literature. Formamide has been condensed by the simple action of gaseous hydrogen chloride passed through a mixture of the amide and the aldehyde, which resulted in the formation of *o*-nitrobenzal-bisformamide (Riedel[4]). More recently, Glazer and Frisch[5] mention having prepared

o-nitrobenzylidene-diacetamide and -dibenzamide by condensing the aldehyde and the amide in alcoholic solution by mere addition of a little hydrochloric acid. For the present study seven different amides have been condensed with *o*-nitrobenzaldehyde, under a variety of conditions. Pyridine trace appeared to be innocuous, doing neither good nor harm, except occasionally when it produced a little resin. The product in all cases was of the bisamide type. In the majority of cases the yield was about 50 %, but heptamide gave almost theoretical yield.

The nitrobenzylidene-bis-formamide obtained by our method was identical with Riedel's, whose experiment was repeated and the two products were compared by their single and mixed melting-points. The *o*-nitrobenzylidene-bisacetamide prepared by our method melted at a slightly higher temperature than that given by Glazer and Frisch. But there was a considerable disparity between the melting-points of the bisbenzamide obtained by us and the dibenzamide reported by the same two workers. Thus our product melted at 251–52° and their product is reported to melt at as low a temperature as 217–18°. We have not so far succeeded in repeating their experiment but analysis as well as molecular weight determination are in favour of the purity and identity of our product.

The products obtained by the condensations with propionamide, *n*-butyramide, *n*-heptamide and phenylacetamide are new.

Experimental

Condensation with Formamide.—(i) 2 g. aldehyde and 1·2 g. formamide were mixed in a flask and 0·08 c.c. of pyridine added (1 : 2 : 0·15 mol.) and the whole was heated on a water-bath at 50–60° for five hours. The mass was then extracted with water to remove formamide and then with ether to remove aldehyde that may have remained. A pale brown product remained, which when recrystallised from dilute acetone came out as pale yellow micro-crystals (needles) melting at 162°, and thus showing that they were not yet pure. Yield about 40%.

(ii) 1 g. aldehyde and 0·6 g. formamide were heated on the water-bath at 60–70° for eight hours. The mass soon became a straw-coloured liquid and bubbling was also noticed. Small, very pale yellow crystals gradually separated. At the end they were thoroughly washed first with cold water and then with ether: after recrystallisation from aqueous alcohol, the bis-formamide came out in white needle crystals, m.p. 177°. Yield about 40%.

(iii) Riedel's experiment was repeated, and 0·5 g. of the aldehyde and 0·3 g. of formamide were mixed and a stream of dry hydrogen chloride

passed: the mass soon melted to a clear liquid as heat was evolved: after about ten minutes solidification took place; the gas was passed for about one hour, the product was taken out as before and recrystallised from hot water. The yield was about 40%, and the m.p. 177°. The mixed melting-point of this product with that obtained in exp. (ii) was also 177°.

The temperature of the water-bath gave a brown colour to the product. That the reaction was quick was shown by another experiment in which the aldehyde and the amide in proper proportions were just heated together till they became a homogeneous liquid. The two were then left together at room temperature for three weeks. About 33% yield was obtained from this.

Condensation with Acetamide.—Acetamide did not condense so easily, not even at full water-bath temperature. But condensation took place when heated for six hours at 130–40°, with a trace of pyridine or without it; the yields in each case being about 48%.

o-Nitrobenzylidene-bisacetamide came out in white silky needles (from hot alcohol) and melted at 235°. Glazer and Frisch[5] give 231–32°. Nitrogen, found 16·49%; the nitrobenzylidene-bisacetamide $C_{11}H_{13}O_4N_3$ requires 16·73%.

Condensation with Propionamide: o-Nitrobenzylidene-bispropionamide.—(i) 2 g. aldehyde and 2 g. propionamide were heated alone on water-bath for seven hours. The mass treated as usual gave no product. There was no action.

(ii) The same were heated at 130–40° for four hours. During this time copious evolution of water-vapour took place and at the end white crystals began to make their appearance in the hot liquid. After cooling, extracting as usual and recrystallising from hot alcohol, the bispropionamide came out in white lustrous long needles, which softened at 218° and melted at 223–25°. Yield 37·9%.

(iii) The same experiment, repeated, but the heating extended to eight hours, made the reacting mass set to a white solid in the flask. The yield was 1·7 g. or 46%.

(iv) The same experiment with a trace of pyridine and the heating being four and eight hours respectively in two different lots, gave an identical yield of 1·8 g. or 48·7%.

(v) When a trace of piperidine was tried, even at water-bath temperature, and in eight hours heating, the mass had become dark red resin which defied all attempts at purification. Probably still lower temperatures might have been more suitable.

The *o*-nitrobenzylidine-bispropionamide is fairly soluble in alcohol and acetone, but not in ether: it melts at 223–25°. (Found: N, 14·80; the bispropionamide $C_{13}H_{17}O_4N_3$ requires 15·05%.)

Condensation with n-*Butyramide*: o-*Nitro-benzylidene-bis*-n-*butyramide.*—As this amide sublimes very much when heated with the aldehyde, a small amount of glacial acetic acid was added to prevent its escape from the reacting mass. Thus, 0·75 g. aldehyde, 0·9 g. *n*-butyramide and 0·5 c.c. of glacial acetic acid were mixed and heated at 110° for six hours. The white solid left was treated with water, washed with ether and recrystallised from alcohol. The bisbutyramide came out in long white needles, melting at 181°. It weighed 1·0 g. or the yield was = 65·1%. It did not decolourise Baeyer's reagent, nor bromine water. (Found: N, 13·81; $C_{15}H_{21}O_4N_3$ requires 13·68%.)

Condensation with Heptamide: o-Nitrobenzylidene-bisheptamide.—0·75 g. of the aldehyde and 1·3 g. of heptamide were heated together for six hours at 105–10°. The mass first melted to a clear liquid and began to solidify after three hours. At the end of the heating, the white solid was extracted with a little cold alcohol to remove the unchanged reactants and the residue was recrystallised from alcohol: the white needles melted at 135° and weighed 1·9 g. (Found: N, 10·93; the bisheptamide $C_{21}H_{33}O_4N_3$ requires 10·74%.) Yield = 97·1%.

Condensation with Benzamide: o-Nitrobenzylidene-bisbenzamide.—There was very little reaction at the water-bath temperature. 4 g. aldehyde and 6·5 g. amide (1 : 2 mol.) were heated together on an oil-bath at 130–40° for four hours. The molten mass soon set to a white solid, after giving out water vapours. On cooling it was extracted with methyl alcohol, and the residue recrystallised from acetone plus alcohol. White needles, melting at 251–52°. Yield = 5·4 g. or 54%.

When heated with a trace of pyridine in the same way, the mass was extracted with acidulated water and then with methyl alcohol. Yield = 52%. The crystals were insoluble in ether and methyl alcohol: and fairly soluble in acetone and ethyl alcohol. (Found: N, 11·43; the bisamide $C_{21}H_{17}O_4N_3$ requires 11·65%. Molecular weight, Rast: 370·8; Expected 375.)

Condensation with Phenylacetamide: o-Nitrobenzylidene-bisphenylacetamide.—2 g. aldehyde and 3·6 g. the amide (1 :2 mol.) were heated at 130–40° for four hours. Water vapours were given out and the mass set to a solid, which was washed first with water and then with ether. Recrystallised from alcohol, the product came out in long white needles, m.p. 229–30°. It was sparingly soluble in the usual organic solvents. Yield = 2 g. or 37·5%. In

another experiment the heating was continued for eight hours, when the yield improved to 2·5 g. or 46·9%.

When the condensation was carried out in the presence of a trace of pyridine, the yield, with four hours' heating, was the same, *viz.*, 2 g. (Found: N, 10·55; the bisamide $C_{23}H_{21}O_4N_3$ requires, 10·42%; Found: Mol. weight, 406·5; calc. 403.)

Summary

o-Nitrobenzaldehyde has been condensed with seven different amides, by heating them together by themselves or with a trace of pyridine. Pyridine is found to be neither helpful nor harmful in these cases. The condensation-product in every case has been of the benzylidene*bis*amide type. The yields were quite fair, ranging from 40 to 65%, and were nearly quantitative in the case of heptamide.

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HETEROCYCLIC COMPOUNDS

Part XVI. Coumarins from Hydroquinone Derivatives

By R. D. Desai and C. K. Mavani

(From the Department of Chemistry, St. Xavier's College, Bombay)

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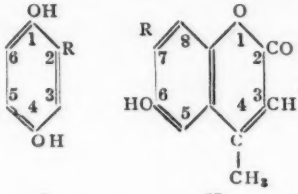
Borsche[1] observed that hydroquinone condensed with aceto-acetic ester and α-methyl-aceto-acetic ester in the presence of concentrated sulphuric acid giving 6-hydroxycoumarin derivatives, though the yield in the latter case was very poor. Desai and Ekhlas[2] attempted the condensation of quinacetophenone (2-acetyl-hydroquinone) without obtaining any definite result, but it is now observed that this condensation does not take place under the influence of any condensing agent. This divergency led us to examine the condensation of 2-chloro-2-bromo-, 2-methyl-, and 2-ethyl-hydroquinones with aceto-acetic and benzoylacetic esters. So far as aceto-acetic ester is concerned, it is found that 2-bromohydroquinone is unreactive, while 2-chlorohydroquinone is less reactive and 2-methyl and 2-ethyl-hydroquinones are more reactive than hydroquinone itself. Benzoylacetic ester does not condense with hydroquinone, 2-chlorohydroquinone, 2-bromohydroquinone and quinacetophenone, but does so readily with 2-methyl- and 2-ethyl-hydroquinones.

Thus we can conclude that the capacity of hydroquinone for undergoing the Pechmann-reaction (H_2SO_4) is reduced partially by the chlorine group, and completely by bromine, and acetyl groups, but is increased by methyl and ethyl groups. This is borne out by the readiness with which 2-methyl- and 2-ethyl-hydroquinones form coumarins with benzoylacetic and α-methyl-, α-ethyl-, and α-propylaceto-acetic esters.

As for the constitutions of these 6-hydroxy-coumarins from 2-substituted hydroquinones (I), and aceto-acetic ester we have assumed the substituent R (where R = Cl, CH_3 or C_2H_5) to occupy the *7* position, as these groups, being *P—O* directing will activate most probably position *5* of the hydroquinone nucleus. The chances for the activation of position 3 are less probable owing to steric considerations, and for the activation of 6 still less probable. Hence the coumarins will have the general formula (II) (where R = Cl, CH_3 or C_2H_5). Their alkaline solutions resemble those of 5-hydroxy-coumarins in being yellow and non-fluorescent, in contrast with those of

7-hydroxy-derivatives which are colourless and fluorescent. Their acyl as well as carbomethoxy derivatives do not undergo the Fries migration, whereas 5- as well as 7-acetoxy-derivatives respond to this reaction.



I II III

The nitration of 6-hydroxy-4-methylcoumarin has been studied by Borsche (*loc. cit.*) who obtained mono- as well as dinitrocoumarins. The mono-nitro coumarin may be either 5- or 7-nitro derivative, more probably the former, as owing to the fixation of the double-bond between the benzene and pyrone rings according to Rangaswamy and Seshadri[3] the hydrogen attached to the carbon carrying a double-bond will be activated. However, our attempts to replace the nitro group by hydroxyl through the usual processes did not succeed. We also coupled benzene diazonium chloride with the alkaline solution of 6-hydroxy-4-methyl coumarin, but the probable azo-compound (III) thus obtained could not be converted into the dihydroxy-coumarin derivative. However, we are still continuing our efforts in order to synthesise the hither-to-unknown 5:6-dihydroxy-coumarins by this process.

Experimental

6-*Hydroxy*-4-*methylcoumarin* was prepared by a slight modification of Borsche's method using 73 per cent. sulphuric acid and hydroquinone diacetate. It crystallised from alcohol in straw-yellow needles, m.p. 240°. (Yield = 30 per cent.)

The Methylether prepared by treating the alkaline solution of the coumarin with dimethyl sulphate crystallised from alcohol in colourless needles, m.p. 169°. (Found: 69·2; H, 5·4; $C_{11}H_{10}O_3$ requires C, 69·5; H, 5·3 per cent.)

The Carbomethoxy derivative obtained by treating the alkaline solution of the coumarin with chloro-carbonic ester, crystallised from dilute alcohol in colourless needles, m.p. 139°. (Found: C, 61·4; H, 4·5; $C_{12}H_{10}O_5$ requires C, 61·5; H, 4·3 per cent.)

It did not undergo the Fries migration when heated in presence of anhydrous aluminium chloride. Similarly the 6-acetoxy derivative did not undergo this reaction under any condition. Finally 6-*benzoyloxy* 4-*methyl coumarin* which was prepared by the action of benzoyl chloride on the parent

coumarin and which crystallised from alcohol in lustrous needles, m.p. 125°, was converted into the original compound when heated in presence of anhydrous aluminium chloride. (Found: C, 72·6; H, 4·5, $C_{17}H_{12}O_4$ requires C, 72·8; H, 4·3 per cent.)

Coupling of benzenediazonium chloride with 4-mehyl-6-hydroxycoumarin.

Formation of 6-hydroxy-5-benzene-azo-4-methylcoumarin (III).—Diazotised aniline (2·8 g.) was added drop by drop to a cold, alkaline solution of the coumarin (3·6 g. in 20 c.c. of 10 per cent. NaOH) with continuous stirring. A small quantity of the precipitate which did not melt was rejected, and the alkaline solution on acidification gave a solid which crystallised from alcohol in brownish-red flakes, m.p. 285° (decomp.). (Found: N, 10·2; $C_{16}H_{12}O_3N_2$ requires, N = 10·0 per cent.) The same compound was obtained by using sodium carbonate in place of sodium hydroxide.

Preparation of 2-acetyl-hydroquinone.

Three methods were tried. The Nencki process (Yield = 10 per cent.), the Friedel-Craft process (yield = 35 per cent.) and the Fries transformation of hydroquinone diacetate (yield = 60 per cent.). It crystallised from alcohol in yellowish needles, m.p. 206°, and its alcoholic solution gave green colouration with ferric chloride. It did not condense with ethyl aceto-acetate either in presence of sulphuric acid or phosphoryl chloride or aluminium chloride.

Clemmensen Reduction of 2-acetyl-hydroquinone to 2-ethylhydroquinone.

A mixture of 2-acetyl-hydroquinone (10 g.), amalgamated zinc (30 g.) and dilute hydrochloric acid (100 c.c.) was heated on sand-bath under reflux for 5 hours. The cooled solution was extracted with ether, dried and the substance recovered. The residue crystallised from benzene in colourless lustrous needles, m.p. 112°. (Yield = 55 per cent.)

Condensation of 2-Ethylhydroquinone with β-ketonic esters.

4-Methyl-7-ethyl-6-hydroxycoumarin was obtained by keeping the solution of 2-ethylhydroquinone (2·6 g.) and aceto-acetic ester (2·6 g.) in 73 per cent. sulphuric acid for 24 hours and pouring over ice. The solid crystallised from alcohol in colourless needles, m.p. 200°. (Yield = 45 per cent.) (Found: C, 70·4; H, 6·1; $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9 per cent.) This coumarin as well as the others which follow resembled 6-hydroxy-4-methylcoumarin in solubility, and other chemical properties.

The Acetyl derivative crystallised from alcohol in needles, m.p. 133°. It did not undergo the Fries migration by heating in contact with anhydrous

aluminium chloride. (Found: C, 68·0; H, 5·9; $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7 per cent.)

3: 4-*Dimethyl*-7-*ethyl*-6-*hydroxycoumarin* obtained from the above phenol and α-methyl aceto-acetic ester crystallised from alcohol in needles, m.p. 239°. (Yield = 40 per cent.) (Found: C, 71·3; H, 6·6; $C_{13}H_{14}O_3$ requires C, 71·5; H, 6·5 per cent.)

The Acetyl derivative crystallised from alcohol in needles, m.p. 150°. (Found: C, 69·7; H, 6·4; $C_{15}H_{16}O_4$ requires C, 69·8; H, 6·2 per cent.)

3:7-*Diethyl*-4-*methyl*-6-*hydroxycoumarin* prepared from α-ethyl aceto-acetate crystallised from alcohol in long, lustrous needles, m.p. 229°. (Yield = 35 per cent.) (Found: C, 72·2; H, 7·1; $C_{14}H_{16}O_3$ requires C, 72·4; H, 7·0 per cent.)

The Acetyl derivative crystallised from alcohol in white, silky needles, m.p. 102°. (Found: C, 69·8; H, 6·8; $C_{16}H_{18}O_4$ requires C, 70·0; H, 6·6 per cent.).

3-*Propyl*-4-*methyl*-6-*hydroxy*-7-*ethylcoumarin* obtained from α-propyl-aceto-acetic ester crystallised from benzene in colourless needles, m.p. 218°. (Yield = 5–10 per cent.) (Found: C, 72·9; H, 7·6; $C_{15}H_{18}O_3$ requires C, 73·1; H, 7·4 per cent.)

4-*Phenyl*-6-*hydroxy*-7-*ethylcoumarin* obtained from benzoylacetic ester crystallised from alcohol in colourless needles, m.p. 194°. (Yield = 15 per cent.) Its alkaline solution was yellow, and non-fluorescent. (Found: C, 76·4; H, 5·5; $C_{17}H_{14}O_3$ requires C, 76·7; H, 5·3 per cent.)

Condensation of 2-*methylhydroquinone with* β-*ketonic esters.*

4: 7-*Dimethyl*-6-*hydroxycoumarin* obtained from 2-methylhydroquinone (2·5 g.) and aceto-acetic ester (2·5 g.) crystallised from alcohol in needles, m.p. 208°. (Yield = 70 per cent.) (Found: C, 69·3; H, 5·5; $C_{11}H_{10}O_3$ requires C, 69·4; H, 5·3 per cent.)

The Acetyl derivative crystallised from alcohol in colourless needles, m.p. 207° (depressed to 185° by the original coumarin). (Found: C, 66·9; H, 5·4; $C_{13}H_{12}O_4$ requires C, 67·2; H, 5·2 per cent.)

3: 4: 7-*Trimethyl*-6-*hydroxycoumarin* obtained from α-methylaceto-acetic ester crystallised from alcohol in lustrous needles, m.p. 267°. (Yield = 45 per cent.) (Found: C, 70·4; H, 6·1; $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9 per cent.)

The Acetyl derivative crystallised from alcohol in needles, m.p. 189°. (Found: C, 68·0; H, 5·9; $C_{14}H_{14}O_4$ requires C, 68·3; H, 5·7 per cent.)

3-*Ethyl*-4: 7-*dimethyl*-6-*hydroxycoumarin* prepared from α-ethylaceto-acetate crystallised from alcohol in colourless needles, m.p. 242°. (Yield = 25 per cent.) (Found: C, 71·4; H, 6·8; $C_{13}H_{14}O_3$ requires C, 71·5; H, 6·5 per cent.)

The Acetyl derivative crystallised from alcohol in silky needles, m.p. 153°. (Found: C, 69·5; H. 6·5; $C_{15}H_{16}O_4$ requires C, 69·8; H, 6·2 per cent.)

3-*Propyl*-4 : 7-*dimethyl*-6-*hydroxycoumarin* obtained from α-propylaceto-acetic ester crystallised from alcohol in white, lustrous needles, m.p. 236°. (Yield = 20 per cent.) (Found: C, 72·1; H, 7·1; $C_{14}H_{16}O_3$ requires C, 72·4; H, 7·0 per cent.).

The Acetyl derivative crystallised from alcohol in white needles, m.p. 102°. (Found: C, 69·9; H, 6·8; $C_{16}H_{18}O_4$ requires C, 70·0; H, 6·6 per cent.)

4-*Phenyl*-6-*hydroxy*-7-*methylcoumarin* prepared from benzoylacetic ester crystallised from alcohol in lustrous needles, m.p. 250°. (Yield = 45 per cent.) (Found: C, 76·1; H, 5·1; $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8 per cent.)

The Acetyl derivative crystallised from alcohol in lustrous needles, m.p. 202°. (Found: C, 73·2; H, 5·1; $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·8 per cent.)

4-*Methyl*-6-*hydroxy*-7-*chlorocoumarin* prepared from 2-chlorohydro-quinone and aceto-acetic ester crystallised from alcohol in colourless, silky needles, m.p. 198°. (Yield = 20 per cent.) (Found: Cl, 16·8; $C_{10}H_7O_3Cl$ requires Cl, 16·9 per cent.)

The Acetyl derivative crystallised from alcohol in needles, m.p. 182°. (Found: Cl, 14·8; $C_{12}H_9O_3Cl$ requires Cl, 15·0 per cent.)

We take this opportunity to thank Rev. Father A. M. Coyne, S.J., the Principal, and late Prof. R. N. Bhagwat for thier kind interest in this work.

Summary

The condensation of β-ketonic esters with hydroquinone, quinaceto-phenone, 2-chloro-, 2-bromo-, 2-methyl-, and 2-ethylhydroquinones in presence of 73 per cent. sulphuric acid shows that the presence of acetyl and bromo groups exert inhibitory effect, while methyl and ethyl groups exert the accelerating effect on the Pechmann Reaction, when present in the hydroquinone molecule. The effect of chlorine group is to reduce the activity to a slight extent.

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UMBILICAL PROJECTION

By Sahib Ram Mandan
(*Lecturer, University of the Panjab*)

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The object of this paper is *to illustrate the use of umbilical projection** to get theorems, relating to centres of similitude and circles of antisimilitude of pairs of circles in a plane, which are usually treated metrically.

Let us start with a quadric Ω in S_3 space of three dimensions.

1. Two plane sections of Ω lie on two quadric cones whose vertices, S_1, S_2 lying on the polar line w.r.t. Ω of the line common to the planes are separated harmonically by the pairs of points where the line S_1S_2 meets Ω and the pairs of the given planes and also by the pair of poles p, q of the given planes w.r.t. Ω. The polar planes s_1, s_2 of S_1, S_2 are then conjugate for Ω, *i.e., the unique point pair*† S_1, S_2 *in polar to* Ω *lying in* pq *is derived.* These can be easily verified.

2. Given three plane sections of Ω, we obtain,‡ from the three poles p, q, r of these planes w.r.t. Ω, three point-pairs of the type S_1, S_2 of §1 on qr, rp, pq being all in polar to Ω and therefore to the plane section by pqr of Ω; these must be the three pairs of opposite vertices of the quadrilateral in the plane pqr with the property that all conics inscribed to it are inpolar to the section by pqr.

3. Given four plane sections of Ω, the six such point pairs‡ are obtained from the poles p, q, r, s of the planes w.r.t. Ω which having all $p\,q\,r\,s$ as self-polar tetrahedron are in polar to Ω; hence they are the singular members of the net of quadric envelopes inscribed in a unique pair of tetrahedra which form a desmic system with $pqrs$. Hence the six-point pairs are the vertices of the desmic system *conjugate*‡ *to this desmic system.*

4. As a special case of what is said in §3, if $pqrs$ is circumscribed to Ω, there is one and only one other tetrahedron $p'q'r's'$ desmic to $pqrs$ and circumscribed to Ω and the third tetrahedron of the desmic system is self-polar w.r.t. Ω.‡

A synthetic proof of it can be had and that is an instructive one.

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* Representation of a quadric upon a plane as explained in H. F. Baker's *Principles of Geometry*, Vol. IV, Chaps. I and II.

† The common idea running through the process in §§ 1, 2, 3 is due to the Referee.

‡ Vaidyanathaswamy, "A memoir on the Cubic Transformations associated with a desmic system," *J.I.M.S. Supplement*, 1927, 1-9, 50.

On projection we have the following results:

1′. Given two circles, their centres of similitude S_1', S_2' are double points of the involution determined by their centres and their limiting points. These circles are inverse w.r.t. two circles s_1', s_2' having their centres at S_1', S_2' called their circles of antisimilitude. s_1', s_2' are mutually orthogonal and are coaxal with and equally inclined to the given circles.

2′. Given three circles, the six centres of similitude arising from them lie by threes on four lines. Their six circles of antisimilitude arrange themselves by threes into four coaxal families which are orthogonal to the circle that cuts the given circles orthogonally. It is a well-known result.

3′. Given four circles, let S_i' $(1 \leqslant i \leqslant 12)$ be the twelve centres of similitude and s_i' the corresponding circles of antisimilitude arising from them; *then S_i' group into three tetrads inscribed in a cubic, constituting a Hesse configuration of three quadrangles in acyclic quadruple perspective. Such that a point of one and that of a second are collinear with a point of the third tetrad. There are sixteen such collinear triads four through each S_i'. These sixteen lines are sides of twelve quadrilaterals, six through each S_i'. These quadrilaterals group into three tetrads such that a quad. of one tetrad and that of a second have a side common with a quad. of the third tetrad. Each line is a side of three quadrilaterals one from each tetrad. Each quad. contains six S_i' as its vertices.*

s_i' group into three tetrads such that a circle of one and that of a second are coaxal with a circle of the third tetrad. There are sixteen such coaxal families which are orthogonal by fours to twelve circles say t_j' $(1 \leqslant j \leqslant 12)$. t_j' also group into three similar tetrads: the sixteen coaxal families arising from them are orthogonal by fours to the twelve circles s_i' and each of these families is orthogonal to a family of the former sixteen. Each t_j' is orthogonal to six s_i' and each s_i' to six t_j'. Every circle belongs to four coaxal families.

4′. As a special case of what is said in §3′, *consider the four circles circumscribed to the four triangles formed by four given points. Their twelve circles of anti-similitude concur* by sixes at eight points which group into two tetrads, one consisting of the given points, the other consists of the inverses of any one of the given points,* w.r.t. *the four circles touching the three circles through this point*; for in this case eight of the twelve circles t_j' of §3 degenerate into point-circles.

The work for this paper was carried through with the help of a Research Scholarship from the University of the Panjab.

* Prof. F. C. Auluck got it analytically.

CHEMICAL INVESTIGATION OF INDIAN LICHENS

Part IV. Constitution of Montagnetol

By V. Subba Rao and T. R. Seshadri
(*From the Department of Chemistry, Andhra University, Waltair*)

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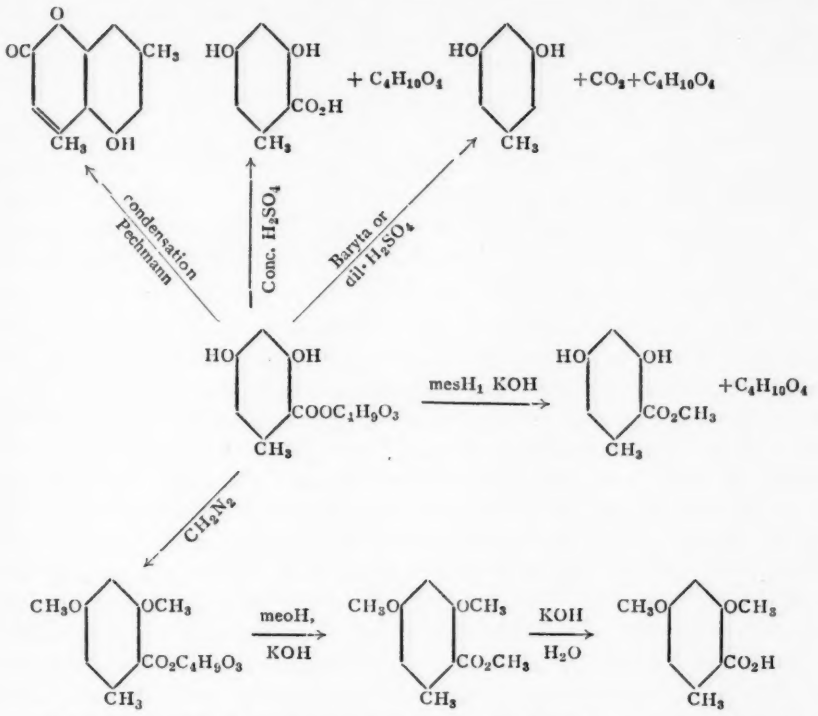
The isolation of a new phenolic component of *Rocella montagnei* named "Montagnetol" was described in Part III of this series.[1] After further careful purification and analysis its composition was found to agree more closely with the formula, $C_{12}H_{16}O_7$. Though the substance did not give the homofluorescein reaction quickly as does orcinol, when the solution was allowed to stand for a few days the characteristic fluorescence developed. There was thus an indication that montagnetol is a derivative of orcinol. This was supported by the fact that 4: 7-dimethyl-5-hydroxy coumarin was formed, when it was treated with ethylacetoacetate under the conditions of Pechmann's reaction. The idea was followed up by subjecting the compound to the action of aqueous baryta and methyl alcoholic potash and analysing the products of decomposition. Decomposition with boiling aqueous baryta took place very readily yielding barium carbonate, orcinol and (meso) erythritol. With methyl alcoholic potash, however, the methyl ester of orsellinic acid was produced along with erythritol. Further by the action of concentrated sulphuric acid in the cold, pure samples of orsellinic acid and (meso) erythritol could be obtained. Dilute sulphuric acid in the cold had no action on the compound; but when the mixture was boiled, decomposition resulted, orcinol and erythritol being formed. From all these data it could be deduced that montagnetol is a compound of orsellinic acid and erythritol and since it is a neutral body it should be the erythrityl ester of orsellinic acid. That none of the phenolic hydroxyl groups are involved in any combination with erythritol was established as follows:—

Montagnetol was methylated with excess of diazomethane and the product was directly treated with methyl alcoholic potash. By this means the dimethyl ether of methyl orsellinate was obtained and this on hydrolysis yielded dimethyl ether of orsellinic acid. It is therefore definitely established that the above conclusion regarding the constitution of montagnetol is correct. The reactions taking place can be represented as below:



The discovery of montagnetol and a knowledge of its constitution bring out prominently a number of interesting features: (1) Orsellinic acid has so far not been detected in lichens though depsides containing this unit are common. It has now been shown that its ester with a sugar alcohol occurs in appreciable quantities. Obviously the instability of the free acid and the stability of the ester account for this phenomenon; (2) Though methyl esters of lichen acids are known to occur fairly frequently in nature, montagnetol seems to be the first definite instance of ester formation with a sugar alcohol. In this connection analogy between montagnetol and the esters of digallic acid with glucose (involving the alcoholic hydroxyl groups) which are widely present in gallotannins may be pointed out.

Experimental

Properties of Montagnetol.—Some of the properties of montagnetol have already been described in a previous communication. It has been stated therein that it does not give the homofluorescein reaction readily when heated with chloroform and alkali. However, it was noticed that the solutions, when

kept for a number of days, gradually developed the characteristic greenish-yellow fluorescence. Montagnetol formed no precipitates with lead acetate, either basic or neutral. With bleaching powder it gave a bright red colour similar to that given by orcinol, lecanoric acid and erythrin. Potassium permanganate solution and Fehling's solution were both reduced by the compound. The colour of Schiff's reagent was not restored. The compound was slightly bitter to taste. A pure sample melted at 156–57°. It crystallised from acetone-benzene mixture as large rectangular tablets; when mounted with a drop of water on a slide they appeared as lense-shaped crystals. [Found: C, 53·0; H, 5·8; $C_{12}H_{16}O_7$ requires C, 52·9; H, 5·9%.]

Condensation of montagnetol with aceto-acetic ester.—A mixture of montagnetol (1 g.) and aceto-acetic ester (3 c.c.) was cooled in freezing mixture, treated with concentrated sulphuric acid (4 c.c.) and left for 24 hours at 0°. The reaction product was then poured into ice-water with good stirring. A slimy substance was obtained, which could be filtered only very slowly. It could not be crystallised and obtained pure. It was therefore treated with 10 c.c. of potassium hydroxide (10%) and left at the room temperature for 24 hours. The solution was then acidified and the precipitated solid filtered and recrystallised from alcohol, when it was obtained in the form of long fine needles melting at 257–58°. The compound gave no colour with ferric chloride, and dissolved only partly in sodium carbonate solution and completely in sodium hydroxide, with a yellow colour. It was found to be identical with an authentic specimen of 5-hydroxy-4: 7-dimethyl coumarin, the mixed melting point being undepressed.

Fission of montagnetol with baryta water.—Montagnetol (0·5 g.) was refluxed with baryta water (8%, 20 c.c.) for 2 hours. A bulky precipitate separated out in 5 minutes and did not dissolve subsequently. It was filtered off and washed with small quantities of water. It was found to be in the form of fine, small needles and was identified as barium carbonate.

The filtrate from above was shaken with ether, but the ether did not extract any material. The aqueous solution was then rendered slightly acid with dilute sulphuric acid and the precipitated barium sulphate filtered off. The filtrate was repeatedly extracted with ether and then neutralised by treatment with excess of barium carbonate. The ether extracts were combined and concentrated, when a red viscous liquid (L) was obtained. The aqueous solution obtained after filtering off the barium carbonate and sulphate, was concentrated, whereby a residue (E) was obtained. On washing repeatedly with ether (E) solidified to a red mass; when a sample of this was treated with a drop of water on the porous plate it became colourless

and melted at 121°. It crystallised from water in the form of hexahedral prisms and possessed a sweet taste and was found to be identical with meso-erythritol by comparison with an authentic specimen. Yield: 0·2 g.

The red viscous liquid (L), on being inoculated with a small crystal of orcinol, quickly turned into a crystalline solid. It was in the form of needles and melted at 55–57° C. and gave the homofluorescein reaction. Mixed melting point with an authentic specimen of orcinol was undepressed. Yield: 0·2 g.

Fission with methyl acloholic potash.—Montagnetol (0·5 g.) was dissolved in methyl alcoholic potash (4%—20 c.c.) and the solution refluxed gently for two hours on a water-bath. Care was taken to see that the temperature of the bath did not rise above 70° C. The solution was then diluted with an equal volume of water and shaken with ether. No material was, however, extracted by the ether. The aqueous portion was then acidified with hydrochloric acid and again ether extracted. The ether extract was separated and concentrated when a brownish-yellow solid was obtained. On treatment with sodium bicarbonate solution only a very small portion went into solution while the rest was undissolved. The mixture was filtered and the insoluble residue washed thoroughly with water. The solid was then recrystallised from acetone, when it was obtained in the form of rhombic crystals which when spread on a microscope slide and treated with a drop of methylated spirit appeared as bundles of long flat needles. It gave a violet colour with ferric chloride and melted at 140–42°. [Found: C, 54·1; H, 6·4; $C_9H_{10}O_4$, H_2O requires C, 54·0; H, 6·0%.] From these results the compound was identified as methyl orsellinate. Its identity was further established by comparison with a pure specimen obtained from lecanoric acid by following the same method of treatment.

The bicarbonate solution obtained above was acidified and extracted with ether. The ether extract on concentration yielded a very small amount of a sticky residue from which no pure product could be isolated.

Fission with cold concentrated sulphuric acid.—Montagnetol (0·2 g.) was dissolved in cold concentrated sulphuric acid (1 c.c.) and the solution kept overnight in the refrigerator. It was then poured into a small quantity of ice-cold water (10 c.c.) and the precipitated solid filtered off and washed well with water. When recrystallised from acetone-ether-benzene mixture, it was obtained in the form of clusters of needles melting at 176° with decomposition. [Found: C, 51·9; H, 5·4; $C_8H_8O_4$, H_2O requires C, 51·6; H, 5·4%.] It gave a violet colour with ferric chloride and was found to be a carboxylic acid, carbon dioxide being briskly evolved from a solution of

sodium bicarbonate when the substance was added to it. From these reactions and the analytical values the compound was identified as orsellinic acid and was found to be identical with an authentic specimen of orsellinic acid obtained by the above method of hydrolysis from lecanoric acid.

Action of dilute sulphuric acid on the compound.—There was no change when montagnetol was treated with cold dilute sulphuric acid, but it underwent degradation when the hot acid was employed, as indicated below:

Montagnetol (2 g.) was refluxed with 7% sulphuric acid (30 c.c.) for 6 hours on the wire-gauze and after cooling, the solution was ether extracted. The ether extract on concentration gave orcinol, which was identified by the homofluorescein reaction and by comparison with an authentic specimen. The aqueous solution was neutralized by treatment with excess of barium carbonate and the solid filtered off. On concentration, the filtrate gave a sticky solid which could be separated into two fractions. A portion went into solution in a mixture of acetone and ether (1 : 1) and on concentrating the solution, was obtained in the form of colourless crystals melting at 154°. This was found to be the unchanged montagnetol. The other portion, insoluble in acetone-ether mixture, melted at 120–22° after purification by recrystallisation from acetone and was found to be identical with an authentic specimen of meso-erythritol.

Methylation of montagnetol with diazomethane.—Montagnetol (1·0 g.) was dissolved in the minimum quantity (20 c.c.) of absolute methyl alcohol and to this solution excess of ethereal diazomethane (1·5 g. contained in 100 c.c. of ether) was added in small quantities at a time during the course of two days. The mixture was kept at the room temperature for about a week. The liquid was then filtered and the solvents distilled off. A viscous liquid was left behind and it could not be converted into a crystalline condition. It gave no colour with ferric chloride either in the aqueous or alcoholic solution.

The viscous liquid was treated directly with 20 c.c. of methyl alcoholic potash (4%) and the solution refluxed gently on a water-bath for 2 hours. The contents were then diluted with an equal amount of water when the clear solution became turbid, with the separation of an amorphous white solid. The whole mixture was, however, ether-extracted and the ether solution cencentrated when a viscous pale yellow liquid was obtained. The aqueous solution was now acidified and again ether-extracted when some more of the viscous liquid was obtained. The two portions were mixed and gently heated on the water-bath for about 15 minutes with 10 c.c. of 5% sodium hydroxide; about 5 c.c. of alcohol were added to obtain complete solution of the substance. The liquid was left overnight when a small

amount of resin separated. It was filtered off and the filtrate ether-extracted whereby a small amount of an oily impurity was also removed. The aqueous portion was then acidified and again extracted with ether. The ether extract on concentration yielded a crystalline solid which after recrystallisation from alcohol appeared as colourless prisms and melted at 140–41° with decomposition. It gave no colour with ferric chloride and was acidic in nature. [Found: C, 60·6; H, 6·2; $C_{10}H_{12}O_4$ requires C, 61·2; H, 6·1%.] The acid was therefore identified as the dimethyl ether of orsellinic acid (melting point given in the literature is 140° with decomposition). The yield was almost quantitative.

Summary

The constitution of montagnetol has been established as the erythrityl ester of orsellinic acid for the following reasons: (1) it gives the homofluorescein reaction slowly, (2) 5-hydroxy-4: 7-dimethyl coumarin could be obtained as a product of its condensation with ethylacetoacetate under the conditions of Pechmann's reaction, (3) decomposition with hot dilute sulphuric acid or with hot baryta produces orcinol and erythritol, (4) concentrated sulphuric acid at 0° gives orsellinic acid and erythritol, (5) hot methyl alcoholic potash converts it into methyl orsellinate and erythritol, and (6) by the action of diazomethane followed by methyl acloholic potash dimethyl ether of methyl orsellinate is obtained.

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SCATTERING OF LIGHT IN BINARY LIQUID MIXTURES

By D. Venkateswara Rao

(From the Department of Physics, Andhra University, Waltair)

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1. Introduction

Krishnan[1] discovered that while for all pure liquids, ρ_u and ρ_v are each less than one and ρ_h is equal to unity,* in binary and ternary liquid mixtures at their critical solution temperatures, in some associating liquids and optical glasses and in colloids and emulsions $\rho_h > 1$. Krishnan concluded from this result that in liquid mixtures at their critical solution temperatures and in optical glasses, the molecules should exist as clusters having sizes comparable with the wave-length of light. About the same time, Rousset[2] reported some quantitative data regarding the light scattering in binary liquid mixtures. He strove to explain the greater intensity of the horizontal component in the scattered light by postulating the existence in such mixtures of intense and depolarised secondary scattering. He has shown that fair agreement exists between the values of ρ_h experimentally found for certain sizes and shapes of the illuminated liquid medium and those calculated on the basis of his theory. Mookerjee[3] has confirmed Rousset's experimental results. Parthasarathy[4] recently came forward with the view that the Krishnan effect is not a genuine molecular phenomenon but that it arises from ignoring the convergence correction of the lenses employed to concentrate incident light into the liquid mixture. According to him, the theory of Gans[5] in respect of the convergence errors is quite adequate to account for the observed anomaly.

From the foregoing, it is clear that, while the experimental fact that ρ_h departs from unity in critical liquid mixtures is well established, the explanations offered by different observers are very different. A thorough experimental examination of each of the explanations offered seems highly desirable. The investigations described in this paper have been carried out from this point of view.

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*ρ_h in this paper always represents the ratio of the intensity of the horizontal component to that of the vertical component. The term *departure* will be used to denote the quantity $(\rho_h - 1)$.

2. *Experimental Details and Results*

A mixture of carbon disulphide and methyl alcohol is studied in the present investigation. An Abney rotating sector photometer, constructed in this laboratory, has been employed in the usual manner for the measurement of intensities. The liquid mixtures are contained in spherical bulbs 2 cm. in diameter which have been painted black on the outside leaving suitable apertures for the ingress of incident light and emergence of the scattered light. The intensity of the light scattered in each mixture is determined relative to that in the 10% one taken as unity.

Results relating to the dependence of ρ_u, ρ_v and ρ_h on concentration are given in Table I. Fig. 1 is a graphical representation of these results. Table II contains the results of intensity measurements.

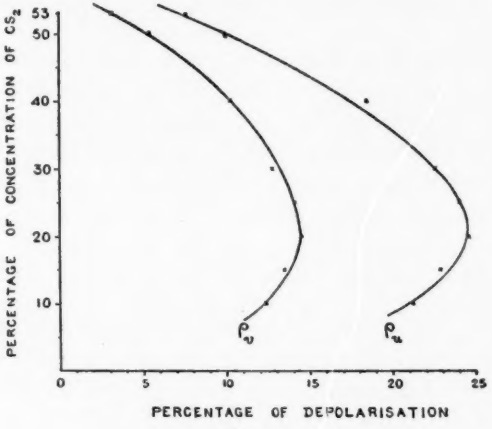

FIG. 1

TABLE I

Dependence of ρ_u, ρ_v and ρ_h on Concentration

Temperature °C.	% of CS_2 in mixture	ρ_v%	ρ_h%	ρ_u%	
				Experimental	Calculated
29	10	12·4	100	21·2	22·1
30	15	13·6	100	22·9	23·9
28·5	20	14·7	100	24·7	25·6
30	25	14·2	100	24·1	24·9
28	30	12·9	100	22·7	22·8
28	40	10·4	100	18·5	18·8
28	50	5·4	100	10·1	10·2
28	53	3·2	141	7·7	6·2

TABLE II

Relative Intensities of Light Scattered in Various Mixtures

% of CS_2 in mixture	I	ρ_u%	I_0	$I_0 + I_d$	I_d	I_c
10	1·0	21·2	0·4	1·0	0·6	0
20	1·7	24·7	0·7	1·7	1·0	0
30	2·7	22·7	1·1	2·5	1·4	0·2
40	3·9	18·5	1·6	3·2	1·6	0·7
50	9·8	10·1	2·0	3·9	1·9	5·9
53	24·0	6·2	3·0	4·2	1·2	19·8

The symbols I, I_0, I_d and I_c are employed to denote the intensities of the total scattering experimentally found, the orientation scattering, the density scattering and the concentration scattering respectively.

Owing to the unavailability of complete data regarding the necessary constants for the binary mixtures studied, I or I_d could not be calculated theoretically. From the fact that the orientation scattering is depolarised to the extent of 6/7, the intensity of that scattering could be determined with the help of the relation

$$I_0 = \frac{13}{6} \cdot \frac{\rho_u}{1+\rho_u} \cdot I$$

the values of ρ_u being taken from Table I.

The values of $I_0 + I_d$ could be computed with the help of the scattering powers of carbon disulphide and methyl alcohol by assuming an additive law. These have been given by Bhagavantam[6] as 13·0 and 0·46 respectively relative to that of benzene taken as 3·2. In the mixture of 10% concentration, it is assumed that I_c is zero. I would then be equal to $I_0 + I_d$. Knowing I_0, $I_0 + I_d$ and I, both I_c and I_d could be easily found out for higher concentrations. The values of I_0, I_d and I_c so found are given in Table II.

As it is considered that any possible formation of large groups brought about by increasing the concentration of a mixture to the critical value, should be attended by noticeable changes in the intensity distribution in the wing, a study is also made of this aspect of the subject. Mookerjee[3] did some work on these lines. On comparing the intensity distribution in the rotational spectrum of the critical solution mixture at the critical temperature of carbon disulphide and methyl alcohol with that in a 30% solution, he failed to find any noticeable changes in the wing accompanying λ 4047 relative to the Raman line at 655 $cm.^{-1}$ The author has examined the intensity distribution in the wings accompanying λ 4358 in mixtures other than the

critical one and compared it with that in the critical mixture at the laboratory temperature. The fall of intensity with $\Delta\nu$ is shown graphically in Fig. 2.

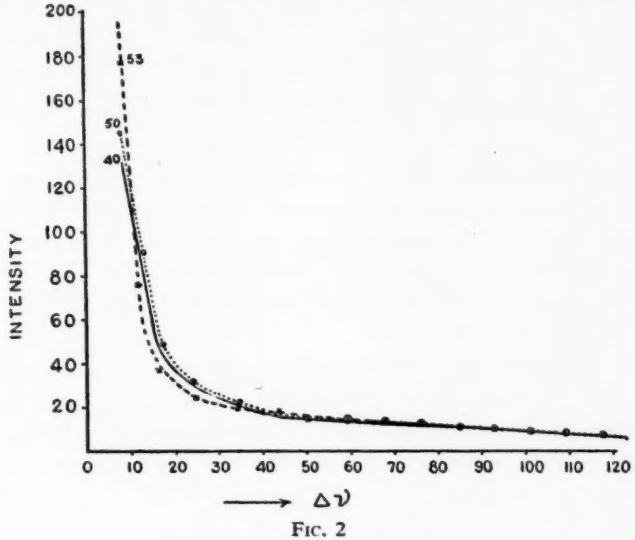

FIG. 2

3. *Discussion of Results*

The relationship between the depolarisation factors ρ_u and ρ_v and concentration is seen very well from Fig. 1. Almost all the plotted points lie on smooth curves, roughly parabolic in shape. The results show that the concentration scattering begins to be felt at a concentration of about 20%. It may further be noted that all concentrations upto 50% show that $\rho_A = 100\%$ while for the critical mixture it has been found that $\rho_A = 141\%$ after making the necessary correction for convergence. That this departure is a genuine effect and that it cannot be ascribed either to secondary scattering or convergence errors will be clear from the two following sections.

A comparison of I with $I_0 + I_d$ shows that, for the 10% and 20% mixtures, the total scattering can be explained as simply the sum-total of the orientation scattering and the density scattering. Increase of concentration beyond this value makes the observed scattering more intense than can thus be accounted for. This surplus intensity has to be ascribed to local fluctuations in concentration and is the ' concentration scattering ', I_c.

The results regarding the rotational Raman effect reveal the significant fact that after 16 cm.$^{-1}$, the curve for the critical mixture shows an unmistakable diminution in intensity relative to the other two curves for the 50%

and 40% mixtures respectively which very nearly coincide. This observation is readily explained if we postulate the existence of molecular swarms in the critical mixture. The increase in size of the scttering centre as the composition is made critical must necessarily produce a wing which is more intense in the neighbourhood of the centre rather than at larger distances.

4. The Effect of Secondary Scattering on Depolarisation Measurements

Rousset's view-point will be examined in this section. He has developed a theory[2] which shows that the anomaly in the depolarisation of the light scattered by critical mixtures has its origin in the asymmetry of the primary scattering with respect to the axis of observation. According to him if the volume illuminated is perfectly symmetrical with respect to all the axes, one should find that $\rho_h = 1$.

When the illuminated volume is of the shape of a disc with its flat surfaces parallel to the horizonal plane, the radius of the disc being R and its vertical depth 2D, ρ_h which is given by (1), should always be greater than unity when D is smaller than R.

$$\rho_h = \frac{1}{4} + \log_e \frac{R}{D}. \qquad (1)$$

When the illuminated volume is a rectangular parallelopiped with its edges equal to $2a$, $2b$ and $2c$ along OX, OY and OZ, then if $a = c$, $\rho_h = 1$ and its departure therefrom is governed by the ratio $\frac{c}{a}$. OX, OY and OZ are respectively parallel to the direction of incidence, of observation and the vertical. These three cases will now be examined experimentally. The relative merits of the cornu method and the diaphragm method are also considered. The critical mixture of carbon disulphide and methyl alcohol at the room temperature of 31° C. and sunlight are used in this part of the investigation. Other arrangements are the usual ones.

Tables III and IV contain the results obtained while studying the dependence of depolarisation on b and c.

TABLE III

Effect of Change of Depth 'c' on Depolarisation

2a cm.	2b cm.	2c cm.	V c.c.	ρ_u%	ρ_v%	ρ_h	a/c
4·8	2·5	0·5	6·0	8·2	3·5	1·43	9·6
4·8	2·5	0·4	4·8	7·2	2·6	1·8	12
4·8	2·5	0·3	3·6	6·6	2·7	2·06	16
4·8	2·5	0·2	2·4	6·5	2·0	2·15	24
4·8	2·5	0·1	1·2	6·5	2·0	2·16	48
4·8	2·5	0·05	0·6	6·5	2·0	2·19	96

TABLE IV

Effect of Change of Breadth 'b' on Depolarisation

2*a* cm.	2*b* cm.	2*c* cm.	V c.c.	Mean θ	ρ_h
4·8	2·5	0·5	6	50° 7′	1·43
4·8	2·0	0·5	4·8	49° 40′	1·40
4·8	1·5	0·5	3·6	49° 45′	1·40
4·8	1·0	0·5	2·4	49° 32′	1·37
4·8	0·5	0·5	1·2	49° 45′	1·40
4·8	0·3	0·5	0·7	50° 8′	1·43

Dependence of ρ_h on the method of observation is shown in Table V. In the Cornu method, the entire track of the scattered light is split up into its components by a double-image prism. All the observations given in Tables III and IV are made by the Cornu method. In the diaphragm method, large volumes of the medium are illuminated and a small aperture is introduced on the observation side. The light let out by it alone is split up by the double-image prism. The components into which it is split are viewed against a uniformly dark background. Observations are made for different values of 2*c* between 2·5 cm. and 0·5 cm. and for different values of 2*b* between 2·5 cm. and 1·5 cm.

TABLE V

Depolarisation Measurements by the Diapharagm Method

2*a* cm.	2*b* cm.	2*c* cm.	V c.c.	ρ_h diaphragm method	ρ_h Cornu method	*a*/*c*
4·8	2·5	2·5	30	1·39	..	1·9
4·8	2·5	2·0	24	1·38	..	2·4
4·8	2·0	2·0	19·2	1·38	..	2·4
4·8	2·5	1·0	12·0	1·44	..	4·8
4·8	2·5	0·5	6·0	1·41	1·43	9·6
4·8	2·0	0·5	4·8	1·41	1·40	9·6
4·8	1·5	0·5	3·6	1·40	1·40	9·6

Dependence of ρ_h on the depth when the illuminated volume is of the shape of a circular disc is given in Table VI. Observations are made by the Cornu method.

The value of ρ_h when the volume illuminated is spherical is given in Table VII. For this purpose a spherical bulb of diameter 2·5 cm., is immersed in a cubical glass vessel containing water so as to minimise errors arising out of its sphericity. The bulb is completely bathed in the illuminating beam.

Observations are made by the diaphragm method. The side of the cubical vessel facing the incident light is adjusted to be normal to the direction of incidence.

TABLE VI

Effect of Change of Depth of Disc-shaped Illuminated Volume

Diameter of the disc = 2·5 cm.; Area of the circular face = 4·9 sq. cm.

2D cm.	V c.c.	Mean θ	ρ_h Obs. ($\tan^2\theta$)	ρ_h calc. (Rousset)	R/D
0·4	2·0	50° 20′	1·5	2·4	6·3
0·3	1·5	53° 36′	1·8	2·8	8·3
0·2	1·0	54°	1·9	3·2	12·5
0·1	0·5	54° 38′	2·0	4·1	25·0
0·05	0·25	57° 7′	2·4	4·9	50·0

TABLE VII

Spherical Illuminated Volume

Radius of sphere	Volume c.c.	Mean θ	Experimental ($\tan^2\theta$)	Theoretical (Rousset)
1·25	8·18	51° 43′	1·40	1·00

According to Rousset, when $2a$ and $2c$ are the same, ρ_h must be unity and its departure depends on the ration $\frac{a}{c}$, being large when $\frac{a}{c}$ is large. Krishnan's view, however, is that whatever the shape of the illuminated mixture, provided its volume is sufficiently small, secondary scattering would be negligible. If now we fix $\frac{a}{c}$ and change only b we would be changing the illuminated volume V while maintaining $\frac{a}{c}$ constant. If Rousset's theory is correct, ρ_h should not vary with b, while if Krishnan's view is correct, ρ_h should vary with b. The results given in Table IV show that wnen $2a$ and $2c$ are kept constant at 4·8 cm. and 0·5 cm. respectively, change of V from 6 c.c. to 0·7 c.c. does not sensibly affect ρ_h at all. These results support Rousset and show that ρ_h is a function not of the size but of the shape of the illuminated volume with respect to the axis of observation. The results given in Table III fully support this view.

Krishnan also stated that the diaphragm method of observation adopted by Mookerjee is likely to lead to high values of ρ_h. The author has examined this statement experimentally. The results are given in Table V. The valucs

of ρ_h found by the Cornu method given in the last but one column agree remarkably well, with those obtained by the diaphragm method, given in the preceding column.

Quantitatively, however, Rousset's theory does not show much agreement with facts. In Table VI are given the values of ρ_h experimentally found by illuminating circular discs of the mixture of different vertical depths. In the same table are given the values of ρ_h calculated with the help of Rousset's theory (relation 1). Though here again ρ_h is seen to be a function of $\frac{R}{D}$, the agreement between the observed and the calculated values is very poor. The expression used in calculating is based on the assumption that the primary scattering is completely polarised. This assumption is probably incorrect. The results can only be explained if we assume that there is in the light scattered, primary cluster scattering in addition to the secondary scattering, the former being responsible for a certain part of the departure $(\rho_h - 1)$ and the latter for the rest. Only the latter varies with $\frac{a}{c}$, becoming large when $\frac{a}{c}$ is large.

If the above conclusion that there is cluster-scattering in the scattered beam is correct, there must be a departure observed even when the illuminated volume is spherical. Under these conditions of experiment, while according to Rousset's theory ρ_h must be unity, the observed value is 1·4 (Table VII). This shows beyond doubt that there is genuine molecular clustering in the critical mixture.

The results given in Tables III and V show another notable feature. When $\frac{a}{c}$ is very large, the dependence of ρ_u, ρ_v and ρ_h on the asymmetry of the illuminated volume is small. ρ_u and ρ_v do not seem to change from 6·5% and 2·0% respectively while ρ_h seems to lie at about 2·2 though $\frac{a}{c}$ changes from 24 to 96. Again, a variation of $\frac{a}{c}$ from 1·9 to 2·4 does not affect ρ_h which remains almost constant at 1·38. The conclusions may therefore be reached that Rousset's theory holds good only when the asymmetry of the illuminated volume is not too great or too small.

It is thus clear that the asymmetry for the illuminated volume undoubtedly influences the depolarisation factors in accordance with Rousset's theory but not to the extent predicted. The results obtained can be satisfactorily explained by postulating the existence of not only depolarised

secondary scattering but depolarised primary scattering also, which can only arise from molecular swarms. This conclusion is supported by the departure observed when the illuminated volume has absolutely no asymmetry whatever.

5. The Effect of Convergence on Depolarisation Measurements

It is now well known that the use of a lens when making depolarisation measurements involves a departure from transversality and this has to be corrected for to arrive at the true depolarisation factors. According to Gans[5] and Ananthakrishnan,[7] the relationships between the semi-angle of convergence of the incident beam, and the various depolarisation factors, when the scattering particles are of molecular dimensions, are given by the following equations

$$\rho_u = \rho_{u_0} + \frac{\theta^2}{2} \quad (2); \qquad \rho_v = \rho_{v_0}' + \frac{\theta^2}{4} \quad (3); \qquad \rho_h = 1 + \frac{1}{\rho_{v_0}} \cdot \frac{\theta^2}{4} \quad (4).$$

Ananthakrishnan has tested (2) experimentally but (3) and (4) have not been verified so far. Parthasarathy[4] assumed (4) to be valid and suggested that the Krishnan effect arises out of ignoring the convergence correction. It is first necessary to verify if formulæ (3) and (4) are valid for pure liquids and for critical binary liquid mixtures. The author has carried out these investigations with two pure liquids, namely, carbon disulphide and carbon tetrachloride. The results, which are not given here, are in complete accord with equations (3) and (4). Such observations have been extended to the critical mixture of carbon disulphide and methyl alcohol and the results are given in Table VIII.

TABLE VIII

ρ_v and ρ_h in Binary Liquid Mixture

Aperture ratio	θ		ρ_v			ρ_h		
	Radian	Degrees	ρ_v%	Correction	ρ_{v_0}%	ρ_h	Correction	ρ_{h_0}
$\frac{F}{2\cdot8}$	0·18	10° 14′	2·63	0·8	1·83	1·32	0·44	0·88
$\frac{F}{4}$	0·13	7° 12′	2·4	0·4	2·01	1·29	0·2	1·09
$\frac{F}{5\cdot6}$	0·09	5° 7′	2·4	0·2	2·2	1·31	0·09	1·22
$\frac{F}{8}$	0·07	3° 35′	2·4	0·1	2·3	1·37	0·04	1·33
$\frac{F}{11}$	0·05	2° 52′	2·4	0·05	2·35	1·39	0·02	1·37
$\frac{F}{16}$	0·03	1° 48′	2·4	0·02	2·38	1·39	0·01	1·38

If these formulæ be deemed applicable to the critical mixture of the author, one must expect ρ_{v_0}% to be a constant quantity and ρ_h to be unity.

The results in Table VIII show that this is indeed far from being the case. These facts at once suggest the presence in the scattered light of something else in addition to convergence effect. It can only be secondary scattering. It is difficult to say precisely how the latter affects the depolarisation when the illuminated volume is of the shape of two cones joined together at their apexes. But on the lines of the conclusions reached in the last section, it would seem reasonable to expect, since increasing convergence means increasing symmetry about the axis of observation, that the depolarisation of the secondary scattering would be large for small angles of convergence and *vice-versa*. If, for a moment, we regard that the theory of convergence also holds for critical liquid mixtures, we must expect that ρ_h must be maximum for the smallest angle of convergence and minimum for the largest angle of convergence, whereas ρ_v must behave in the reverse way. Results of the experiment are in accordance with what we actually expect.

The effect of convergence seems, however, to be not exactly to enhance ρ_{v_0} and ρ_h. If, indeed, its effect is to enhance them, ρ_h must be increased from about 1·0 for 1° 48′ to 1·44 for 10° 14′. The secondary scattering present must further enhance ρ_h at 10° because of the asymmetry of the 10° beam. In no case should we expect ρ_h to fall below the enhanced value, due even to convergence alone. The actual value is not adequate even to explain the convergence error, for ρ_h, for the 10° convergence is only 1·32. If the convergence error is regarded as positive and taken away from this $\rho_{h_0} = 0{\cdot}88$, that is much less than unity. This is very surprising.

We know with certainty that the effect of secondary scattering is always to enhance and never to diminish ρ_h. So that, even if convergence did not produce any error at all, the secondary scattering itself must make ρ_h greater than unity because even for an angle of convergence of 20°, the asymmetry of the scattered beam with respect to the direction of observation is very large. But what we do not know is whether the convergence error is really positive, as for pure liquids. An assumption that it is negative explains the unmistakable *diminution* of ρ_h from 1·39 to 1·29 as the semi-angle of convergence is *increased* from 1° 48′ to 7° 12′. This must also be the reason why ρ_h diminishes to the surprisingly low value of 0·88 on making a positive correction.

6. *Summary*

The isothermal variation of ρ_u, ρ_v and ρ_h with concentration in mixtures of carbon disulphide and methyl alcohol is investigated. It is suggested that the results clearly point to the existence of molecular clustering in the critical composition mixtures at the laboratory temperature. Results obtained with

the rotational Raman effect also support such a view. The theories of secondary scattering of Rousset and Krishnan have been put to experimental tests. An unmistakable dependence of ρ_h on the shape and not the size of the illuminated volume of the mixture is noticed. The departure obtained only when the volume illuminated is spherical, can be attributed wholly to genuine molecular aggregation provided there is no error due to convergence. The diaphragm method of observation is shown to be as good as the Cornu method. The expressions developed by Gans and Ananthakrishnan regarding the relation between ρ_v and ρ_h and the angle of convergence of the incident light are verified in pure liquids. In the critical mixture, the effect of convergence is found to be not to enhance, but to diminish ρ_h from its normal value of unity. Further complications due to secondary scattering are also observed.

The author is deeply indebted to Prof. S. Bhagavantam for his valuable guidance during the progress of these investigations.

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THE DIAMAGNETISM OF THE HALOGENS

By Dr. S. Ramachandra Rao and Mr. S. R. Govindarajan
(*From the Department of Physics, Annamalai University, Annamalainagar*)

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1. Introduction

The study of the magnetic susceptibility of binary mixtures of organic and inorganic liquids has been engaging the attention of many workers in recent years. The conclusions seem to indicate that the additive law of magnetic susceptibilities is generally obeyed except when the two component liquids mix with a chemical reaction.

When molecules combine with each other resulting in the formation of new compounds (very often complex and unstable), deviations from the additive law are noted. Studies in formic acid-water mixtures undertaken by Rao and Sriraman (1938) and Rao and Narayanaswamy (1939) and those in sulphuric acid-water mixtures by Varadachari (1935) have amply justified this conclusion.

These cases do not include solutions of salts in water. Investigations by Rao and Sriraman (1937) have shown that when some salts are dissolved in water, departures from the additive law may be obtained. In these cases, the deviation has been attributed to (*a*) interaction between ions and water molecules, (*b*) depolymerisation of water, (*c*) release of constraints within the molecule due to their breakage into ions and (*d*) change of valency of any of the ions when the salt is dissolved. While the first two causes do not produce more than 1% deviation, the others may be expected to produce comparatively greater departures. Flordal and Frivold (1935) obtained large deviations when some alkaline-earth halides were dissolved in water. Hocart (1929) examined a number of halides and obtained results for dissolved salts at 30 to 60% concentration. He found that the specific diamagnetic susceptibility of the dissolved salts calculated from an application of the additivity law was 2 to 3% higher than the susceptibility of the corresponding solid salts.

Bhatnagar and Lakra (1933) have studied the magnetic properties of iodine in different solvents and find that whereas iodine has a specific susceptibility of about 0·35* in the solid state, the value in solutions of carbon

* All susceptibility values in this paper are diamagnetic and in 10^{-6} unit.

disulphide or benzene is as high as 0·51. This has been explained as due to a tendency for the iodine to ionise in solution, the third of the causes enumerated above.

The study of the magnetic properties of the halogens in solution is of interest in the investigation of dipole moments. Briegleb (1930) has recently found that iodine has a dipole moment of about $1 \cdot 2 \times 10^{-18}$ e.s.u. in solutions of carbon disulphide and benzene, whereas it has no permanent moment in cyclohexane. This has also been explained as due to the tendency for the iodine to ionise in the former solvents and the absence of such a tendency in cyclohexane. In the present work the magnetic susceptibilities of chlorine, bromine and iodine have been studied in detail in such solvents.

The problem of dipole moments as related to molecular compound formation has received little attention. Ebert (Glasstone, 1936) observed that the polymerisation of a mixture of ethyl alcohol and hydrogen chloride was much greater than the sum of the ploymerisations due to the constituents. This result suggests that the two molecules unite, as it is not impossible, to form a highly polar compound. Further it has been found that *s*-trinitrobenzene dissolved in benzene (which is nonpolar) has a definite moment of $0 \cdot 8 \times 10^{-18}$ e.s.u. The value is too large to be due to any experimental error and Bennett (1929) suggests that it is due to the presence of an unstable compound between trinitrobenzene and benzene. Glasstone (1936) observes that all molecular compounds of this type will probably have a high dipole moment because of the addition of a semipolar bond. Some measurements by Veich and Nespital (1931) confirm these anticipations. In this paper an attempt is made to correlate values obtainable on dipole moments of halogens in solutions, with the conclusions drawn from magnetic investigations. In this connection it is relevant to remark that studies in the dipole moments of the nonpolar halogens in polar and nonpolar solvents will go a long way in deciding the validity of the above results and discussions.

The spectra of iodine vapour in different solvent vapours have been studied by Chatlet (1930). When iodine solution in benzene is vapourised at 90° an absorption band is observed belonging neither to iodine nor to benzene vapour. The vapour density of benzene-iodine mixtures was studied and showed a contraction which is attributed to molecular association.

It was believed therefore that a detailed magnetic study of the halogens in solution might be of interest. Thorough purification of the liquids with a view to obtaining reliable and consistent results was the guiding feature of the investigation.

2. *Experiment*

(*a*) *Purification of substances.*

(*i*) *Chlorine.*—Chlorine was obtained by the action of pure distilled hydrochloic acid on pure and fresh bleaching powder. To remove traces of hydrochloric acid, the gas was passed through wash bottles containing distilled water. The traces of water were removed by passing the gas through concentrated sulphuric acid wash bottles. The gas so obtained was frozen below its boiling point and thus uncondensable impurities were removed. Before absorbing the gas in the liquids, it was further dried by being passed over phosphorous pentoxide. Rubber connections were avoided.

(*ii*) *Bromine.*—Bromine was purified by the method of Anantakrishnan and Ingold (1935). " Bromine for analysis " was distilled in an all-glass apparatus over fused potassium bromide to eliminate traces of chlorine. It was then shaken up with concentrated sulphuric acid in a separation funnel several times and left overnight. All traces of water thus removed, the bromine was separated from the acid and distilled fractionally in an all-glass apparatus. The bromine thus obtained was cooled in a mixture of carbon dioxide snow and ether and the uncondensed vapours of bromine hydrides were pumped out through traps of soda lime. The bromine so purified melted at — 7·3° C.

(*iii*) *Iodine.*—Iodine was purified by the method given by Philbrick and Holmyard (1932). Iodine marked " Kahlbaum resublimed " was ground well with small quantities of fused potassium iodide and calcium oxide and heated with a regulated flame in a beaker. Iodine sublimed off and recondensed into shining crystals on the surface of a bulb placed above. The calcium oxide removed any moisture and the dry iodine so obtained was kept in an ungreased sulphuric acid desiccator.

(*iv*) *Carbon disulphide.*—Analytical carbon disulphide was shaken with anhydrous copper sulphate and distilled. The first and last portions (10%) were rejected. The middle portion boiling at a constant temperature of 46·2° C. was used.

(*v*) *Carbon tetrachloride.*—Mercke's pure carbon tetrachloride was shaken with phosphorous pentoxide and left overnight. It was then filtered and distilled, rejecting the first and last portions. The distillate registered a constant boiling point of 77° C.

(*vi*) *Chloroform.*—Analytical chloroform from Mercke was washed with water, then with concentrated sulphuric acid several times to eliminate traces of alcohol. The chemical was then washed a number of times with water until the washings gave no acidic test. It was then shaken up with

calcium chloride and left overnight. It was distilled after filtration, rejecting the first and last portions. The purified specimen boiled at 61·2° C.

(*vii*) *Acetic acid.*—The purification of acetic acid was effected by the method of Orton and Bradfield (1927). 100 gms. of acetic acid " puriss " from Mercke was shaken up with 8·2 gms. of acetic anhydride and 2 grams of chromic oxide and was maintained near the boiling point nearly for half an hour. It was then distilled with a short still head to prevent spurting of the oxide. The first fraction (10–15%) was rejected. It is known that for every 0·1% of water, the melting point of acetic acid is lowered by 0·2° C. The purified specimen had a melting point of 16·6° C., thus indicating that the acid was 100% pure.

(*viii*) *Ethyl alcohol.*—Ethyl alcohol was purified from rectified spirit by the method of Sydney Young (1902). Equal weights of strong spirit and benzene were shaken well and fractionally distilled using a fractionating column. The first fraction containing benzene, water and alcohol, and the second portion containing benzene and alcohol were rejected. The last portion containing alcohol was redistilled. The alcohol so distilled boiled at a constant temperature of 78·3° C. This method is supposed to give very pure alcohol.

(*ix*) *Benzene.*—Analytical benzene from Kahlbaum was shaken up with anhydrous sodium sulphate and left overnight. It was then distilled rejecting the first and last portions. The middle portion boiling at a constant temperature of 80·2° C. was used.

(*x*) *Cyclohexane.*—A very pure sample from Kahlbaum was shaken up with concentrated sulphuic acid and fractionally distilled. The distillate was redistilled, the first and last portions being rejected in both cases. The purified specimen boiled at a constant temperature of 80·1° C.

(*xi*) Water for the standardisation experiments was obtained by repeated distillation, in an apparatus made of pyrex free from any rubber connections.

(*b*) *Preparation of solutions.*

In the case of chlorine solutions, the purified gas was directly absorbed into the solvents. To determine the concentration of the solution, excess of potassium iodide solution was added to a definite volume of the chlorine solution when an equivalent quantity of iodine was liberated. This iodine was titrated against standardised thiosulphate. From these results, the concentration of chlorine in the solution could be calculated. Bromine and iodine solutions were prepared by weighing definite quantities of the halogens and dissolving them in the solvents. From the weight of the

solutions thus obtained the weight of halogen in 100 gms. of solution was calculated. For further concentrations, the solutions were diluted and in each case the concentration computed.

(*c*) *Determination of densities.*

The density in gm. per c.c. at room temperature (about 30° C.) was found by the hydrostatic method.

(*d*) *The determination of the specific susceptibility.*

The specific susceptibility was determined by the Gouy method. The pole faces of the Pye electromagnet used were 3 cm. in diameter and the air gap had a width of 1·25 cm. Water was used as the standard substance. Its specific susceptibility was taken to be 0·720. The tubes which contained the solutions to be investigated had internal diameters of about 8 mm.

3. *Results*

(*a*) *Pure substances.*

(*i*) *The halogens.*—The specific susceptibility of bromine was determined for two specimens after purification. The susceptibility of iodine was determined by the Curie method. The following table shows the authors' values compared with those of other investigators.

TABLE I

Investigators	Bromine χ	Iodine χ
Owen (1912)	0·403	0·360
Honda (1910)	0·375	0·348
Bhatnagar and Lakra (1933) ..	..	0·35
Authors—Stock I	0·347	0·364
Do. Stock II	0·346	..

It will be seen that the values cited for bromine are higher than the authors' values. This must be due to the fact that the bromine used here was specially purified by an exacting process. It had a density of 3·074 at 30° C. which compares very favourably with 3·084 given in the *International Critical Tables* (1928).

(*ii*) *The solvents.*—The susceptibilities for the purified solvents are tabulated below.

TABLE II

Solvents	Density	Authors χ	Other investigators χ
Carbon disulphide	1·252	0·543	0·550* 0·565† 0·540‡
Carbon tetrachloride	1·584	0·438	0·429§
Chloroform	1·483	0·489	0·488§
Acetic acid	1·043	0·530	0·526§
Ethyl alcohol	0·791	0·747	0·732‖ 0·744‡ 0·749¶
Benzene	0·874	0·714	0·712‡
Cyclohexane	0·790	0·804	0·810‡

* Rao and Sivaramakrishnan (1932). † Varadachari (1935).

‡ *Int. Crit. Tables* (1928). § Pascal (1911).

‖ Rao and Narayanaswamy (1939). ¶ Kido (1932).

(*b*) *Bromine solutions.*

(*i*) *Bromine in carbon tetrachloride.*—Bromine and carbon tetrachloride are completely miscible in all proportions. The values are given below. The concentrations of bromine are expressed in percentage by weight in the solution.

TABLE III

Bromine in Carbon Tetrachloride

Serial No.	Concentration	Density (gm. per c.c.)	χ Observed	χ for bromine in solution
1	19·72	1·736	0·420	·35
2	10·95	1·662	0·428	·35
3	7·02	1·633	0·434	·38
4	5·11	1·621	0·435	·38
5	2·78	1·610	0·438	·44
6	0	1·592	0·438	..

It is observed that the specific diamagnetic susceptibility calculated for bromine in the state of solution is not far from the value of 0·347 in the pure state. There is apparent however a tendency for the value to increase when the dilution becomes greater.

(*ii*) *Bromine in chloroform.*—The results are given below.

TABLE IV

Bromine in Chloroform

Serial No.	Concentration	Density (gm. per c.c.)	x Observed	x for bromine in solution
1	21·34	1·681	0·459	·35
2	9·25	1·590	0·478	·37
3	7·52	1·559	0·485	·43
4	5·44	1·541	0·487	·45
5	3·38	1·502	0·488	·46
6	0	1·490	0·489	..

The specific susceptibility of bromine in solution is the same as the value in the free state when the concentration is 21·34. When the concentration is decreased it is found that the specific susceptibility in the state of solution increases gradually. At large dilutions the value appears to approach a limiting value.

(*iii*) *Bromine in acetic acid.*—The acetic acid molecule is known to be highly polar. A study of bromine solutions in acetic acid is therefore of special interest.

TABLE V

Bromine in Acetic Acid

Serial No.	Concentration	Density (gm. per c.c.)	x Observed	x for bromine in solution
1	21·85	1·212	0·494	0·35
2	11·06	1·123	0·514	0·43
3	7·55	1·083	0·527	0·49
4	5·43	1·066	0·529	0·51
5	2·49	1·055	0·530	0·53
6	0	1·049	0·530	..

The specific susceptibility of bromine in solution appears to be larger than in the previous cases.

(*iv*) *Bromine in cyclohexane.*—The cyclohexane molecule has no dipole moment. Experiments show that in this case the specific susceptibility of bromine in solution has the same value as in the free state.

TABLE VI

Bromine in Cyclohexane

Serial No.	Concentration	Density (gm. per c.c.)	χ Observed	χ for bromine in solution
1	7·26	0·845	0·771	0·35
2	6·11	0·838	0·777	0·35
3	5·34	0·832	0·779	0·35
4	4·22	0·825	0·785	0·35
5	3·08	0·817	0·790	0·35
6	2·27	0·810	0·793	0·35
7	1·09	0·801	0·799	0·35
8	0	0·786	0·804	..

(*c*) *Chlorine solutions.*

(*i*) *Chlorine in acetic acid.*—The values for the mixtures could not be calculated from the additive law, since a reliable value for chlorine could not be obtained. But in the last column will be found the values calculated for chlorine in solution. It is interesting to note that in all cases the values are very much higher than the values usually quoted for gaseous chlorine, $-0·57$.

TABLE VII

Chlorine in Acetic Acid

Serial No.	Concentration	Density (gm. per c.c.)	χ Observed	χ for chlorine in solution
1	5·91	1·029	0·542	0·73
2	5·43	1·031	0·541	0·73
3	4·82	1·033	0·540	0·74
4	4·27	1·037	0·539	0·74
5	3·48	1·042	0·538	0·74
6	2·16	1·045	0·535	0·74
7	1·38	1·047	0·533	0·73
8	0	1·049	0·530	..

(*ii*) *Chlorine in chloroform.*

TABLE VIII

Serial No.	Concentration	Density (gm. per c.c.)	χ Observed	χ for chlorine in solution
1	5·61	1·467	0·502	0·71
2	5·12	1·469	0·501	0·72
3	4·34	1·475	0·500	0·74
4	3·04	1·479	0·496	0·73
5	2·41	1·484	0·495	0·74
6	1·20	1·487	0·492	0·74
7	0	1·490	0·489	..

An examination of the last column shows that the calculated value of the halogen is again as high as that observed in the previous case, and the maximum values so calculated are very nearly equal in the two cases.

(*iii*) *Chlorine in cyclohexane.*—Only a dilute solution could be conveniently prepared. The values are shown below.

TABLE IX

Chlorine in Cyclohexane

Serial No.	Concentration	Density (gm. per c.c.)	χ Observed	χ for chlorine in solution
1	3·28	0·775	0·798	0·56
2	2·07	0·784	0·799	0·57
3	1·61	0·788	0·801	0·56
4	0	0·786	0·804	..

The mean value for the halogen in solution is observed to be only 0·563 which is nearly equal to the value ordinarily quoted for chlorine. It should be remembered in this connection that bromine-cyclohexane solutions also obeyed the additive law.

(*d*) *Iodine solutions.*

These solutions are of special interest since it is well known that solutions of iodine in different organic solvents are characterized by different colours. The study of the magnetic properties of iodine solutions from the point of view of their colour was carried out by Courty (1937). He used the Curie-Cheneveau method for the determination of magnetic susceptibility and claims an error not greater than 0·5% in the susceptibility values.

He has inferred from his results that the deviation from the additive law is dependent on the colour of the solution. In the case of violet solutions, he gives a deviation of 0·52%. Average deviations of 0·86%, 1·95% and 4·65% are reported in the cases of brown, red brown and red solutions respectively.

Courty (1937 *a*) also studied the diamagnetism of solutions of iodine in ethyl alcohol and found that the deviations depended largely on the state of purity of the alochol.

The results obtained in the present investigation are given below:—

(*i*) Iodine in carbon disulphide.

TABLE X

(Violet Solutions)

Iodine in Carbon Disulphide

Serial No.	Concentration	Density (gm. per c.c.)	x Observed	x Calculated	x for iodine in solution
1	9·65	1·336	0·528	0·526	0·39
2	8·17	1·321	0·533	0·528	0·42
3	6·78	1·309	0·536	0·531	0·44
4	5·39	1·306	0·539	0·533	0·47
5	4·07	1·293	0·540	0·536	0·47
6	2·79	1·278	0·541	0·538	0·47
7	1·46	1·269	0·542	0·54	0·49
8	0	1·252	0·543	..	..

Average deviation from the additive law = 0·75%.

(*ii*) *Iodine in benzene.*

TABLE XI

Iodine in Benzene

(Red Solutions)

Serial No.	Concentration	Density (gm. per c.c.)	x Observed	x Calculated	x for iodine in solution
1	9·89	0·917	0·689	0·679	0·46
2	8·51	0·904	0·696	0·684	0·50
3	6·35	0·888	0·707	0·692	0·60
4	5·05	0·880	0·709	0·696	0·61
5	3·48	0·874	0·712	0·702	0·66
6	1·98	0·871	0·713	0·707	0·67
7	0	0·870	0·714	..	..

Average deviation from the additive law = 1·6%.

(*iii*) *Iodine in ethyl alcohol solutions.*

TABLE XII

Iodine in Ethyl Alcohol

(Brown Solutions)

Serial No.	Concentration	Density (gm. per c.c.)	x Observed	x Calculated	x for iodine in solution
1	4·76	0·821	0·737	0·729	0·54
2	3·88	0·814	0·739	0·732	0·54
3	2·32	0·799	0·743	0·738	0·57
4	1·08	0·794	0·745	0·743	0·56
5	0	0·791	0·747	..	..

Average deviation from the additive law = 0·8%.

(*iv*) *Iodine in cyclohexane.*

TABLE XIII

Iodine in Cyclohexane

(*Violet Solutions*)

Serial No.	Concentration	Density (gm. per c.c.)	x Observed	x Calculated	x for iodine in solution
1	1·01	0·801	0·800	0·800	0·37
2	0·99	0·800	0·800	0·800	0·37
3	0	0·786	0·804	..	..

Average deviation from the additive law = 0%.

An examination of the last four tables shows that the largest deviation (about 1·6%) from the additive law occurs in the case of benzene. Solutions of iodine in carbon disulphide and carbon tetrachloride show about the same deviation. Cyclohexane solutions follow the additive law.

These results are in substantial agreement with those of Bhatnagar and Lakra (1933). The susceptibility of iodine in solution in all the cases studied, except in the case of cyclohexane increases when it is dissolved. But Courty (1937) finds an opposite conclusion. The observed value of the susceptibility in the case of benzene solutions of iodine appears to be less than the calculated value. The specific susceptibility of iodine in the state of solution is found by Courty to be less than the value in the free state.

There are several points of interest in Courty's results which appear to throw doubt on the main conclusions drawn by him. In a violet solution of iodine in carbon disulphide the calculated value of the susceptibility was 0·552 against the observed value of 0·547; in another violet solution of the same solid in the same liquid, his calculated value is 0·548 against the observed value of 0·552. His results retabulated in the following manner serve to emphasize the discordance of many values.

TABLE XIV

Iodine %	χ Observed	χ Calculated	Difference %	Solvent	Colour
1·14	0·4287	0·4282	0·1	CCl_4	Violet
2·28	0·486	0·485	0·2	$CHCl_3$	,,
5·51	0·547	0·552	0·9	CS_2	,,
7·33	0·552	0·548	0·7	CS_2	,,
10·48	0·538	0·542	0·7	CS_2	,,
6·22	0·736	0·741	0·7	$(C_2H_5)_2O$	Brown
20·37	0·677	0·684	1·02	$(C_2H_5)_2O$	,,
2·35	0·694	0·701	0·9	C_7H_8	Red brown
10·48	0·667	0·681	2·0	C_7H_8	,,
4·13	0·657	0·698	5·8	C_6H_6	Red
8·56	0·658	0·682	3·5	C_6H_6	,,

In the case of carbon disulphide the observed values do not show a progressive change when the concentration is increased. The percentage differences in the cases of carbon tetrachloride and chloroform solutions are much smaller than the probable error in the observed values of the susceptibility. The conclusion of Courty that the change of susceptibility when iodine is dissolved in a solvent has a definite correlation with the colour of the solution appears to us however to have some weight although the data on which the conclusions are based are not sufficient and probably doubtful in some cases.

4. *Discussion*

(*i*) *Probable ionisation in dilute solutions.*—In the present investigation, a striking feature observed was that halogens had a higher value in solution than in the free state except in the case of cyclohexane.

After allowing for all possible sources of error, it may be safely taken that the susceptibility values are correct to within $\frac{1}{4}\%$. Repeated measurements on solutions having the same halogen concentration gave values which were found within the range of error of *not more* than this percentage. Further the Gouy force in the case of each solution was measured three to six times and the mean value was taken. Also in each test, the Gouy forces were determined at 4 field currents and thus four values of the susceptibility were obtained. The tabulated value in the case of each solution is thus the average of 12 to 24 independent measurements, all of which lay within the range of error mentioned above. It is expected that the susceptibility values given in this investigation possess a high standard of accuracy.

The conclusions drawn from such results may be said to be based on firm experimental basis. In the following table, the specific susceptibilities of the halogen elements in the state of solution are collected. The values in the pure state are also given for comparison. It is worth while considering the possible error in the values of the susceptibility of the halogen elements in the state of solution. Consider for example serial number 6 in Table XI. The concentration of iodine in benzene is nearly 2%. The observed susceptibility is 0·713. The susceptibility of the solution calculated on the basis of additivity law is 0·707. The observed value is greater than the additivity value by 0·006. Since the error in the susceptibility value is nearly 0·002, the error in the specific susceptibility of the iodine calculated in the state of solution is $50 \times 0{\cdot}002$ or 0·1. This works to an error of 1·5% in the calculated value of the specific susceptibility of iodine in the state of solution.

If the concentration is about 5% the error in the specific susceptibility for the halogen element in the state of solution is $20 \times 0{\cdot}002$ or 0·04. The error here is just less than 0·7%.

Hence even in the case of concentrations of about 2%, the error in the observed specific susceptibility is not high. At lower concentrations, the error is bound to be higher.

The specific susceptibilities in Table XIV are calculated from the observed susceptibility value at concentrations in the neighbourhood of 5%.

TABLE XIV

Serial No.	Solvent	χ Value for Halogen in Dilute Solution		
		Chlorine	Bromine	Iodine
1	Carbon disulphide	..	..	0·47 0·505†
2	Carbon tetrachloride	..	0·44	..
3	Chloroform	0·74	0·46	..
4	Acetic acid	0·74	0·53	..
5	Ethyl alcohol	..	..	0·57
6	Benzene	..	..	0·61 0·510†
7	Cyclohexane	0·57	0·35	0·37
8	Pure element	0·57*	0·347	0·364

* The value of χ for chlorine is taken from *Int. Crit. Tables*, 6, 354.
† Bhatnagar and Lakra (1933).

A scrutiny of the above table shows that the halogens do not preserve their elemental character in the solvents other than cyclohexane. It would

be of interest to compare the gram ionic values of the halogens in the solutions with the theoretical and experimental values for these ions.

In Table XV the values for the halogens in dilute solutions multiplied by their respective atomic weights have been shown against their actual gram ionic values.

TABLE XV

Serial No.	Solvent	Susceptibility per Gram Atom in the State of Solution		
		Chlorine	Bromine	Iodine
1	Carbon disulphide	..	32·8	59·7
2	Carbon tetrachloride	..	..	..
3	Chloroform	25·5	36·7	..
4	Acetic acid	25·9	40·7	..
5	Ethyl alcohol	..	..	72·4
6	Benzene	..	..	77·4
7	Cyclohexane	19·9	28·0	46·9
	Author	Theoretical values of the gram ionic susceptibility		
8	Pauling (1927)	29·0	54·0	80·0
9	Slater (1929)	25·79	40·01	59·83
10	Angus (1932)	22·86	36·65	55·32
	Author	Experimental values of the gram ionic susceptibility		
11	Joos (1923 and 1925)	19·5	38·3	57·5
12	Kido (1933)	22·1	34·7	53·2
13	Hoare and Brindley (1935) ..	24·2	34·5	50·6
14	Flordal and Frivold (1935) ..	23·6	34·0	51·5

In drawing conclusions from the foregoing table, too much importance should not be attached to the significance of the numerical values in the case of each halogen element since in each case the error in the specific susceptibility value becomes greatly magnified when this value is multiplied by the atomic weight concerned.

What is however of special significance is the fact that the susceptibility of the halogen element in solution (in solvents other than cyclohexane) becomes nearly equal to that of the susceptibility of the ion. In the cases of chlorine and bromine, the coincidence is striking. In the case of iodine, the solution values appear to exceed the ionic values. But in the light of the large errors present in the case of iodine because of its large atomic weight, too much significance need not be attached to the absolute values.

The importance of this discussion is evident when the results of Briegleb (1930) on the dipole moments of iodine in solutions of benzene, carbon disulphide, hexane and cyclohexane are considered. He finds that whereas iodine has a dipole moment of $1 \cdot 2 \times 10^{-18}$ e.s.u. in the first two solvents, it has no permanent moment in hexane or cyclohexane. This may suggest that in benzene and carbon disulphide the electron pair shared between the two atoms tends to be drawn closer to one atom than the other. The iodine atom will thus tend to ionise in these solvents. In cyclohexane on the other hand such is not the case. There is no tendency for the halogen to ionise and hence the dipole moment is zero.

This observation combined with the favourable agreement between the theoretical and experimental ionic values and the values from solutions, seems to point conclusively to the result that the halogens ionise in the organic solvents mentioned, except in cyclohexane wherein they are probably not ionised.

The dipole moments of the halogens in all the solvents do not seem to have been studied. A study of such values should be of special interest.

(*ii*) *Colour of iodine solutions.*—The problem of the colour of iodine in solution has attracted much attention (Mellor, 1922, p. 110). These colours are usually violet and brown, with intermediate tints from violet-red to reddish brown. There seems to be a general tendency for violet solutions to become brown when sufficiently cooled and for the brown solutions to become violet when heated.

It has been suggested that brown solutions contain I_4 molecules and that violet solutions contain I_2 molecules. The relative proportions in the equilibrium equation $I_4 \rightleftharpoons 2I_2$ decide the colour. A change of temperature affects the proportions and thus alters the colour.

However the molecular weight of iodine at the freezing point of the solutions concerned was studied by Beckmann (Mellor, 1922, p. 110). He found that the molecular weight always corresponded to I_2.

The colour of iodine solutions should be due probably to other reasons. There may be partial ionization of the iodine in the state of solution or a partial combination of iodine with the solvent. As a matter of fact, both these causes are likely to operate. The amount of combination between the solvent S and I_2 depends on the particular set of conditions, being represented by the following balanced reaction

$$SI_2 \rightleftharpoons S + I_2$$

In violet solutions, the combination should be very much less than in brown solutions. This kind of combination would obviously produce a change in magnetic susceptibility. The relatively large increase of susceptibility in the case of brown solutions is perhaps due to such a reaction in addition to the possible ionisation.

(*iii*) *Absorption spectra of iodine solutions.*—Walker (1935) studied the absorption spectrum of iodine in organic solvents. He classified such solutions into four broad groups from the point of view of the interaction between the solvent and solute molecules.

(1) Solutions of iodine in inert nonpolar solvents like cyclohexane give the maximum absorption at the same wave-length (516–518 mμ) as for iodine vapour. The interaction between the solvent and solute molecules is due to Van der Waals forces only.

(2) In polar solvents which do not have any chemical interaction for the I_2 molecules, there is an attractive force due to polarisation of the I_2 molecules by the electrical field of the solvent molecules. The wave-length corresponding to maximum absorption is slightly displaced to 490–500 mμ.

(3) When the solvent is unsaturated (*e.g.*, alcohols and ethers), molecular addition compounds may be formed between I_2 and solvent molecules. Maximum absorption in such cases is found to occur at about 440 m. The solutions are red-brown in colour.

(4) When chemical reaction takes place between I atoms and the hydrogen in the solvent resulting in the formation first of HI and then of HI_3, intense bands appear in the absorption spectrum at 350 and 290 mμ, these being characteristic of HI_3. The brown colour disappears gradually in such cases.

The results shown in Table IV fall in line with Walker's classification. In non-polar solvents like cyclohexane, iodine is violet. In polar solvents like ethyl alcohol in which probably a molecular addition compound takes place, the deviation from susceptibility is comparatively larger than in the first case. In the case of benzene, evidence from various sources show that some kind of reaction should take place between iodine and benzene which should bring about an electric moment and a change of colour from violet to brown.

More detailed experiments on solutions of iodine have been carried out in this laboratory by Mr. D. Krishna Iyer and a report will be communicated for publication in due course.

5. *Summary*

The magnetic properties of chlorine, bromine and iodine dissolved in a few organic solvents have been studied. It is observed that in all the cases studied except cyclohexane the magnetic susceptibility of the halogens in dilute solutions is greater than the corresponding value for the free halogen.

The probable causes for such changes are examined. The ionisation of the halogen element and the formation of loose molecular compounds between the solvents and solutes are examined in detail. Magnetic properties are correlated with well-known optical properties of iodine solutions like their colour and absorption spectra.

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FLUORESCENCE, ABSORPTION AND SCATTERING OF LIGHT IN RUBY

By Anna Mani

(From the Department of Physics, Indian Institute of Science, Bangalore)

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1. Introduction

The fluorescence and the pleochroism exhibited by ruby have been the subject of detailed investigations at the hands of many investigators, notably du Fay (1724), Boisbaudran (1887), Crookes (1887, 1889), Miethe (1907), Becquerel (1907, 1910, 1911), Mendenhall and Wood (1915) and Gibson (1916). They have been studied with especial thoroughness by du Bois and Elias (1908) and by Deutschbein (1932, 1934). Reference may also be made to recent papers by Venkateswaran (1935) and Thosar (1938). The fluorescence spectrum consists at room temperatures of two sharp and intense lines at 6927 and 6942 A.U. respectively, accompanied by other bands of varying width and intensity. At ordinary temperatures, these appear at wavelengths longer and shorter than the principal doublet. But at liquid air temperatures the bands towards the shorter wavelength disappear completely from the fluorescence spectrum. At such temperatures, there is no correspondence between the fluorescence and absorption bands except in regard to the principal doublet and certain fainter companion lines which appear on the longer wavelength side of the same. In other words, the Stokes Law is strictly obeyed, only longer wavelength bands appearing in fluorescence and the shorter wavelength bands in absorption.

Despite the numerous investigations mentioned above, the fluorescence spectrum of ruby has not as yet been fully elucidated. The two principal lines are usually regarded as due to electronic transitions in the triply ionized chromium atoms present as an impurity in the crystal. This explanation leaves it obscure why the principal lines do not agree in position and intensity when the nature of the ground material is varied. The fainter components accompanying the principal doublet have been ascribed by Deutschbein to an intra-molecular Stark effect. Why, if this be the case, the companions appear only on the longer wavelength side is unexplained. Further, the diffuse bands have been attributed to the superposition of the molecular

or crystal lattice vibrations on the electronic transitions. This view, however, is unsupported by any independent data regarding the lattice spectrum of the crystal except in regard to one frequency nearly at 415 cm.$^{-1}$, which has been identified in the Raman spectrum of alumina, and agrees tolerably with the frequency shift of the 7138 band in fluorescence.

That the chromium activator forms an integral part of the crystal lattice of the ground material *viz.*, aluminium oxide, is indicated by the fact that the principal lines in emission and absorption are partially polarised (Pringsheim, 1928). Previous investigations on the polarised absorption and polarised excitation of fluorescence are however, confined to the principal doublet. A fuller study of the polarisation characters of the fluorescence and absorption bands as well as the Raman spectrum of the crystal has been carried out and is described in the present paper. The work was undertaken in order to elucidate the origin and nature of the principal, subsidiary and diffuse bands exhibited by ruby, as well as the nature of the arrangement of the Cr^{+++} ions in the ground lattice.

2. *The Lattice Spectrum of Alumina*

The Raman spectrum of alumina has been previously studied by Hibben (1932) who reported four weak lines having frequency shifts of 536, 728, 931 and 1191 cm.$^{-1}$, and by Deutschbein (1932) who could observe only one Raman line at 415 cm.$^{-1}$ Two large crystals of transparent synthetic alumina of dimensions $3{\cdot}5 \times 2 \times 1{\cdot}5$ cms. and $4 \times 2 \times 2$ cms. respectively were used in the present investigation. A two prism glass spectrograph supplied by Adam Hilger, having a dispersion of 28 Å/mm. in the 4358 A.U. region was employed for photographing the spectra. The crystal was immersed in a liquid of nearly the same refractive index, *viz.*, α-bromonaphthalene, to minimise parasitic illumination and diminish the strong continuum due to fluorescence. The spectrum recorded, however, was very weak even after two days of continuous exposure. Two Raman lines having frequency of 412 and 376 cm.$^{-1}$ have been recorded with fair intensity on the plates. The line at 412 cm.$^{-1}$ is stronger than the other. It may, however, be remarked that there are indications of the presence of a few more faint lines in the spectrum. But due to the superposition of the strong continuum, they cannot be listed with certainty.

Coblentz (1908) has reported three maxima in selective reflection for alumina at 11 μ, $11{\cdot}8\,\mu$ and $13{\cdot}5\,\mu$ corresponding to frequency shifts of 909, 847 and 741 cm.$^{-1}$ and it will be seen that they do not coincide with either of the observed Raman lines.

3. *The Absorption Spectrum of Ruby*

The absorption spectrum of the sample of ruby used for the study of fluorescence was obtained using a tungsten filament lamp as the source of continuous radiation. The crystal was placed with its optic axis perpendicular to the direction of observation so that light traverses the crystal in a direction perpendicular to the optic axis, and the ordinary and extraordinary spectra were recorded.

The absorption spectrum in the red consists of a doublet with three bands on the Stokes and six on the anti-Stokes side. The spectrum is reproduced in Fig. 5, and the relative intensities of the different bands in both spectra are given in Table I. It will be seen from a comparison of Tables I and II that the absorption bands correspond closely with those appearing in emission. In the extraordinary spectrum, with the electric vector vibrating along the optic axis, all bands except 6595 and 6693 are very weak. These results are in agreement with those of du Bois and Elias (1908). Three bands in the blue, ascribed by Deutschbein to $^4F \rightarrow {}^2H$ transitions of Cr^{+++}, are also given in Table I, along with their intensities in the two spectra, and re-

TABLE I

The Absorption Spectrum of Ruby

No.	Wave-length	Wave-numbers	Intensities of bands	
			Ordinary	Extraordinary
1	6581	15191	..	..
2	6595	15158	6	5
3	6649	15036	..	..
4	6693	14937	5	2
5	6758	14793	2	0
6	6822	14654	2	0
7	6927	14431	9	2
8	6942	14400	10	1
9	6996	14290	1	0
10	7016	14249	1	0
11	7049	14182	1	0
12	4686	21334	2	6
13	4753	21033	5	1
14	4768	20967	3	5

produced in Fig. 6. The results show that two of these bands *viz.*, 4686 and 4768 A.U. are opposite in behaviour to those in the red region, the intensity of the extraordinary ray for them being greater than the ordinary. The strong

polarisation of these bands had been visually observed by du Bois and Elias.

4. The Fluorescence Spectrum of Ruby

For the observations of the photo-luminescence of ruby, a piece of synthetic ruby, $9 \times 7 \times 5$ mms. cut with its longest edge parallel to the optic axis was employed. The axis was fixed by observing the extinction directions between crossed polaroids and confirmed by viewing it in convergent light between crossed nicols, after cutting it. Light from a pyrex mercury arc was focussed on the crystal by a long-focus lens and the fluorescence spectrum photographed with a Fuess glass spectrograph having a dispersion of nearly 100 Å/mm. in the 6900 A.U. region. The fluorescent light emitted transversely to the incident beam was focussed on the slit of the spectrograph. In experiments with polarised light, a properly oriented nicol was placed between the crystal and the incident beam and a double-image prism was inserted in the path of the fluorescent light. Ilford H.P.2 plates having an H and D number of 2500, and Ilford infra-red plates with H and D 100, sensitized with ammonia were used in photographing the spectra. Wavelengths of the bands were ascertained by measurements with a cross-slide micrometer in comparison with neon lines as standard.

Table II gives the wavelengths and intensities of the bands obtained along with those given by Deutschbein and Venkateswaran. Besides the twenty-four bands observed by Deutschbein, three new bands with centres approximately at 7539, 7544 and 7772 A.U. have been recorded. Further the 7138 band shows a definite doublet structure with components at 7129 and 7147 A.U. respectively. Because of the insensitiveness of the infra-red plates used to the 6000–6900 A.U. region, the bands 6495 and 6430 observed by Venkateswaran could not be obtained. The author's values show fairly good agreement with the rest, considering the low dispersion of the instrument used. It should, however, be remarked that the bands on the Stokes side appear to be sharper in the ruby used in the present investigation than those recorded by Deutschbein. Their intensities as compared with the principal lines also show differences from those given by the latter. The complete fluorescence spectrum of ruby is reproduced in Fig. 1 in the accompanying Plate.

TABLE II

The Fluorescence Spectrum of Ruby

Author—25° C.		Deutschbein—20°			Venkateswaran—35°
Wave-length	Intensity	Wave-length	Intensity	Half-width in cm^{-1}	Wave-length
5900–6700	..	..	..	..	6100–6900
..	..	..	..	..	6430
..	..	..	..	..	6495
6581	1	6583	1	30	..
6595	2	6595	3	40	6592
6649	1	6647	1	50	6650
6693	4	6692	4	80	6690
6758	3	6762	3	70	6753
6802	3	..	..	..	6791
6817	3	6820	3	100	6814
6833	2	..	..	..	..
6927	9	6927	9	16	6927
6942	10	6942	10	19	6945
6978	1	6977	2	18	..
6985	2	6986	4	18	..
6996	2	6996	4	18	6992
7016	4	7017	6	18	7027
7049	6	7049	6	18	7059
7078	6	7072	2	60	7089
7129	7	..	..	..	7125
7147	7	7138	3	60	..
7188	6	7188	2	80	7164
..	..	..	..	..	7222
7275	5	7276	2	60	7266
7324	4	7323	2	60	..
7359	2	..	..	..	..
7440	1	7438	1	100	..
7520	2	7517	1	100	..
7544	2	..	..	..	..
7606	1	7603	1	40	..
7674	1	7675	2	40	..
7725	3	7723	3	100	..
7772	2	..	..	..	..
7924	2	7921	2	100	..

5. *Polarisation of the Fluorescence Bands*

Designating the three mutually perpendicular directions in pace as OX, OY and OZ, where OX is the direction of incidence, OY the direction of observation and OZ the vertical direction perpendicular to the other two, the crystal is set with its optic axis along any one of the three directions for studying the polarisation characters of the bands. For each of the three settings, three separate photographs were taken,

(1) with incident light unpolarised,

(2) with incident electric vector polarised with vibrations along OZ, and

(3) with incident electric vector polarised with vibrations along OY. The fluorescent light was analysed into vertical (OZ) and horizontal (OX) components by means of a double-image prism, and are marked V and H in the figures. The spectra obtained are illustrated in Figs. 2, 3, 4, 7, 8, 9, 10, 11 and 12 in the accompanying Plates.

(*a*) Figs. 2, 3 and 4 give the horizontal and vertical components for unpolarised incident light where the optic axis is respectively along OX, OY and OZ.

(*b*) Figs. 7 and 8 illustrate the spectra with the optic axis along OX and the incident light vector along OY and OZ respectively.

(*c*) Figs. 9 and 10 correspond to the same setting as for *b*, but with the optic axis along OZ.

(*d*) Figs. 11 and 12 correspond to the same setting as for *b*, but with the optic axis along OY.

The directions of the optical vibrations in the incident light and the fluorescent light are indicated, when along OX and OY, by arrows parallel to them and by circles with central dots when along OZ. The optic axis is indicated by a set of three lines parallel to OX and OY when along them and by a triangle with a central dot when along OZ. Taking 20 as the intensity of the strongest band in each plate, intensities of the strong bands have been visually estimated and are given in Table III.

It will be seen from all the figures, that the principal doublet and almost all the bands are very intense when the fluorescent light vector vibrates in the (0001) plane, perpendicular to the optic axis ; *i.e.* in general, the ordinary fluorescence spectrum is stronger than the extraordinary. Moreover, as may be seen from Figs. 7–12, both vertical and horizontal components appear brighter when the incident light vibrates perpendicular to the optic axis than when along it. This becomes intelligible when it is remarked that the absorption of light by ruby is also stronger for vibration-directions perpendicular to the optic axis. Figs. 2, 11 and 12 illustrate the fact that whatever the nature of polarisation of the incident light, with the crystal oriented with its optic axis along OY, both V and H components are equally intense for all the bands. This should be so, because for this particular orientation of the crystal, both components of the fluorescent light vibrate in the (0001) plane. However, the most remarkable fact is that with the incident light vector vibrating along

TABLE III

The Intensities of the Fluorescence Bands in Polarised Excitation

Direction of vibration of Incident Light	Orientation of the Optic Axis along	Components of Fluorescent Light along	Relative Intensities of the Components of the Flourescence Bands															
			6595	6693	6758	6822	6927	6942	7016	7049	7078	7129	7147	7188	7275	7324	7520	7725	7924
YZ Plane	OX	OX	2	1	2	2	12	10	4	4	4	7	8	5	7	4	3	3	2
		OZ	4	5	3	3	17	20	5	7	8	10	10	7	6	5	1	2	1
YZ Plane	OZ	OX	4	6	4	3	17	20	7	8	9	11	11	8	7	6	1	4	4
		OZ	2	2	2	2	12	10	6	5	5	8	8	5	6	4	4	3	1
OZ	OX	OX	1	1	2	2	12	10	4	4	4	8	7	4	6	2	2	1	1
		OZ	2	5	3	3	17	20	3	7	8	9	8	7	6	5	1	3	2
OZ	OZ	OX	3	5	3	3	17	20	3	7	8	9	8	7	6	5	1	3	2
		OZ	2	1	2	2	12	10	4	3	3	7	6	4	5	3	3	4	3
OY	OX	OX	1	1	2	2	12	10	5	4	4	8	8	5	6	5	3	2	2
		OZ	2	4	2	2	17	20	4	6	7	9	9	7	6	6	1	3	1
OY	OZ	OX	3	5	3	3	17	20	4	7	8	10	9	7	6	5	1	4	2
		OZ	2	1	2	2	10	8	4	4	4	7	6	4	5	3	3	3	3

the optic axis, it is the component in fluorescence perpendicular to the optic axis that appears stronger. This may be clearly seen from Fig. 10. In general, whether the incident light vector vibrates along or perpendicular to the optic axis, it is that component vibrating perpendicular to the optic axis that comes out more intensely.

6. *Discussion of Results*

A. The Lattice Spectrum of Alumina.—According to detailed X-ray analysis, the crystal structure of alumina (corundum) is similar to that of calcite, and the unit cell belongs to the space group D^6_{3d} of the holohedral class of the rhombohedral system, having three equal axes making an angle of 85° 42′ with each other. For the purpose of analysing the lattice spectrum of the crystal, we shall consider the fundamental unit cell containing four aluminium and six oxygen atoms. The character table for this is identical with that given by Bhagavantam and Venkatarayudu (1939), and indicates that the thirty degrees of freedom of the atoms are distributed among six representations, four of which are single and two doubly degenerate. Two vibrations of the totally symmetric class and five of the doubly degenerate types are active in the Raman effect, the same being inactive in the infra-red. Besides these seven, there are eleven modes of vibration, nine of which are active in the infra-red and two inactive in both the infra-red and the Raman spectra. Only three of the former have been observed in infra-red absorption.

One of the important facts emerging from the investigations of the Raman spectrum of alumina is its extreme feebleness in spite of the fact that a clear, transparent crystal of large size was available. It has been shown by several authors that the Raman lines connected with ionic bindings are generally of very low intensity. Therefore, the observed weakness of the spectrum of alumina rather suggests that the binding between Al and O atoms is more or less ionic in character.

The strongest of the Raman lines recorded, *viz.*, 412 cm.$^{-1}$ is presumbaly due to one of the two totally symmetric oscillations of the unit cell considered above in which the two aluminium and the three oxygen atoms situated around the cell corners, move towards or away from their common centre.

B. Electronic Transitions of Triply Ionized Chromium.—All chromium phosphors give emission lines in the red, indicating that the lines owe their origin to the chromium activator embedded in the ground lattice isomorphically. Deutschbein (1932) has shown that these characteristic lines of chromium undergo significant changes in wavelength and intensity, with different

metallic oxides and silicates as the basic material. This is also evident from Venkateswaran's work (1935) on emerald (beryllium aluminium silicate) whose principal doublet coincides not with the 6927 and 6942 A.U. bands but with 6802 and 6822 A.U. bands of ruby. This suggests that the 'subsidiary' lines *viz.*, 6802, 6822, 6978, 6985, 6996, 7016 and 7049 together with the principal doublet of 6927 and 6942 A.U. in ruby, are due mainly to electronic transitions of the Cr^{+++} ion. The ground material has thus the effect of suppressing some of the electronic bands and enhancing some others. The principal doublet has been assigned to a transition $^4F \rightarrow {}^2G$ of a $3d$ electron of triply ionized chromium. Deutschbein assumes that the subsidiary bands arise from an intramolecular Stark effect. Candler (1937) has however, pointed out the difficulties inherent in the latter suggestion as it does not explain either the position or the differential intensities of the bands on either side of the doublet. Thosar (1938) has given reasons to believe that the 7016 and 7049 bands have frequencies that agree with the electronic transitions $^4P_{5/2} \rightarrow {}^4F_{5/2}$ and $^4P_{7/2} \rightarrow {}^4F_{7/2}$ of the Cr^{+++} ion respectively. The assignments of these bands to electronic transitions of Cr^{+++} ion is also supported by the observation that the floruescence and absorption bands in the region 6927-7049 overlap.

C. Vibrational Bands of Ruby.—The important role played by the lattice of the ground material in the fluorescence and absorption spectra of ruby becomes clear when we consider the origin of the bands which lie on either side of the electronic bands in ruby. The present investigation shows that at room temperature the Stokes bands are distinctly stronger than the corresponding anti-Stokes bands. The observation of some authors that the anti-Stokes bands are stronger, is obviously due to the insensitiveness of the plates used by them to the longer wave-length region. The relative intensities of the Stokes and anti-Stokes bands observed in the present investigation suggest that they arise from the superposition of the lattice vibrations of alumina on the electronic transitions. Deustchbein was the first to suggest that these bands might arise thus and he explained the band at 7138 A.U., as due to the Raman frequency of 412 $cm.^{-1}$ observed by him, being superposed on the electron jump. It has been shown earlier that there are altogether eighteen normal modes of vibration for the alumina lattice which may modulate the electronic transitions and give rise to fluorescence bands. On the basis of the two Raman frequencies at 412 and 376 $cm.^{-1}$ and the three infra-red frequencies at 909, 847 and 741 $cm.^{-1}$, eight fluorescence bands on the Stokes and anti-Stokes sides of the principal doublet may be satisfactorily accounted for. These assignments are given in Table IV. A perusal of Table IV and the accompanying Plates, shows that more or less perfect mirror

TABLE IV

Wave-length in A.U. at 25° C.	Wave-length in A.U. at −195° C.	Shift in cm.$^{-1}$ from 6934. R_1	Assignments from the Lattice spectrum in cm.$^{-1}$
6595	6586	761	$741 - \nu_3$
..	6620	683	..
6649	6640	638	..
6693	6688	530	..
..	6707	488	..
6758	6744	407	$412 - \nu_2$
6764	6757	378	$376 - \nu_1$
6817	6807	268	..
7078	7067	273	..
7129	7120	377	$376 - \nu_1$
7147	7140	416	$412 - \nu_2$
7188	7178	491	..
..	7196	525	..
..	7260	648	..
7275	7279	683	..
7324	7318	757	$741 - \nu_3$
	7346	809	$847 - \nu_4$
	7404	915	$909 - \nu_5$

image symmetry holds for the bands 6595, 6649, 6693, 6758 and 6817 on the anti-Stokes side and for 7324, 7275, 7188, 7138 and 7078 bands on the Stokes side. It is also possible that besides the principal doublet, the other electronic transitions give rise to vibrational bands in the fluorescence spectrum. This may possibly account for the slight departure from mirror image symmetry about the principal doublet, of the fluorescence and absorption bands observed at liquid air temperature. A more detailed experimental study of the lattice spectrum of alumina is desirable in order to give a complete explanation of the fluorescence and absorption bands exhibited by ruby.

D. Polarisation Characters.—Table I indicates that for all bands except 6595, 6693, 6927 and 6942 of ruby, absorption of light takes place almost exclusively in the ordinary spectrum *i.e.*, in the (0001) plane perpendicular to the optic axis of ruby. This absorption, however, has little effect on the emission spectrum, as may be inferred from Figs. 3, 4, 5, 6, 7 and 8 in which the fluorescence bands come out strongly when the electric vector vibrates perpendicular to the optic axis. Therefore, to a first approximation we are justified in ignoring the effect of absorption on the relative intensities of emission bands in polarised excitation. The principal doublet is strongly polarised, the degree of polarisation of 6942 band being higher than that of the 6927 band. Two other electronic bands *viz.*, 6822 and 7049 A.U. are also polarised to the same extent as the latter while the 7016 A.U. band is depolarised. The continuous spectrum is also polarised to the same extent

and in the same sense as the principal doublet. These polarisation characters of the electronic bands support the suggestion that the Cr_2O_3 activator possesses a preferred orientation of distribution in the ground lattice. The origin of the polarisation of the electronic bands is not well understood. However, in the present investigation it is observed that the fluorescent vibrations appear stronger with the light vector vibrating normal to the optic axis than when along it, whatever be the nature of the polarisation of the incident light vector. This indicates that the phosphorescent centre in ruby is not a simple electric dipole.

From the values of intensities given in Table III, the vibrational bands have been divided into the following groups, and are listed in Table V.

(1) Bands whose polarisation is in the same sense, and equal to or greater than that of the principal doublet.

(2) Bands whose polarisation is opposite to that of R_1 and R_2 *i.e.*, when the vertical component of the latter is more intense than the horizontal component, the horizontal components of the bands are more intense than the vertical and *vice versa.*

TABLE V

Bands polarised in the same sense as R_1 and R_2	Bands polarised in the opposite sense to R_1 and R_2	Bands completely depolarised
I	II	III
6595 ..... $-\nu_3$		
5693		6758 .... $-\nu_1$
7078		7129 .... $+\nu_1$
7147 ..... $+\nu_2$		
7188		7275 ....
7324 ..... $+\nu_3$		
	7520	
7725		
7924		

(3) Bands which are completely depolarised, *i.e.*, the vertical and horizontal components are nearly equal in all settings.

It will be seen from the above table that the Stokes and anti-Stokes components of the vibrational bands show more or less the same polarisation characters in polarised excitation. It may also be seen that the two components of the doublet at 7138 are polarised differently, the 7129 component being depolarised nearly to the same extent as the 6758 band on the

anti-Stokes side, while the component at 7147 A.U., having a frequency shift of 412 cm.$^{-1}$ appears to be more highly polarised. It is obvious that the vibrations which appear polarised in light scattering should give rise to fluorescence bands which are highly polarised, especially as the principal doublet itself is polarised. This agrees with the assignment of the Raman line at 412 cm.$^{-1}$ to the symmetric oscillation. The bands which are completely depolarised and those whose polarisation characters are opposed to that of the principal doublet may be attributed to the degenerate vibrations of the crystal lattice.

In conclusion, the author wishes to express her grateful thanks to Sir C. V. Raman, F.R.S., N.L., for the continued interest he has shown throughout the course of this investigation. My sincere thanks are due to Dr. C. S. Venkateswaran for the valuable help rendered by him.

Summary

The paper deals with the results of a spectroscopic investigation of the fluorescence, absorption and scattering of light in ruby. The first order lattice spectrum of alumina is shown to possess eighteen normal modes of vibrations. Two Raman lines having frequency shifts of 376 and 412 cm.$^{-1}$ have been obtained with a single crystal of alumina. The fluorescence and absorption spectra of ruby have been recorded using specially sensitized infra-red plates to register the bands in the long wavelength region with good intensity. The polarisation characters of the bands have also been studied with reference to the direction of the optic axis of the crystal and the direction of polarisation of the incident beam. From a perusal of the results, the emission bands have been divided into two groups *viz.*, (1) electronic bands caused by transitions of the shielded electrons of Cr^{+++} ion, (2) vibrational bands arising from a modulation of the electronic transitions by the crystal lattice vibrations. The frequency shifts of eight of the vibrational bands from the principal doublets agree fairly well with one or the other of the observed Raman and infra-red frequencies of alumina. The polarisation characters of the bands on the Stokes sides are also in good agreement with those of the corresponding bands on the anti-Stokes side.

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Note.—After the paper had been written, a note by Thosar in the *Physical Review* for October 15, 1941, came to hand which deals with the same subject.

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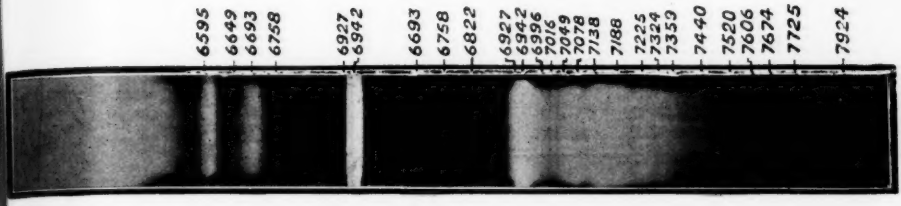


Fig.1

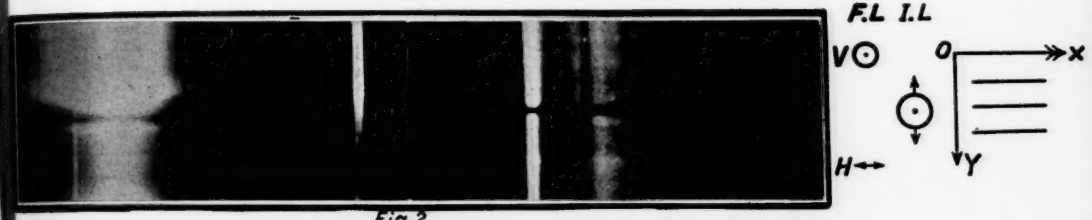


Fig.2

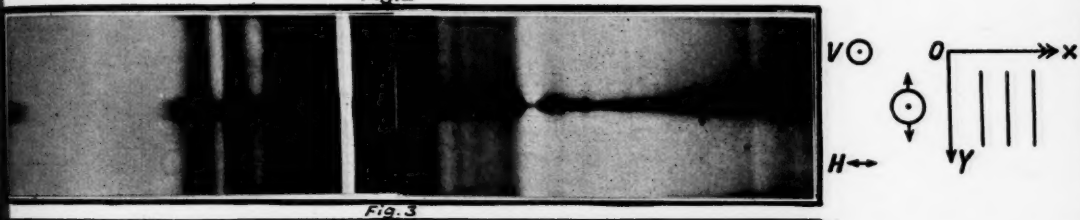


Fig.3

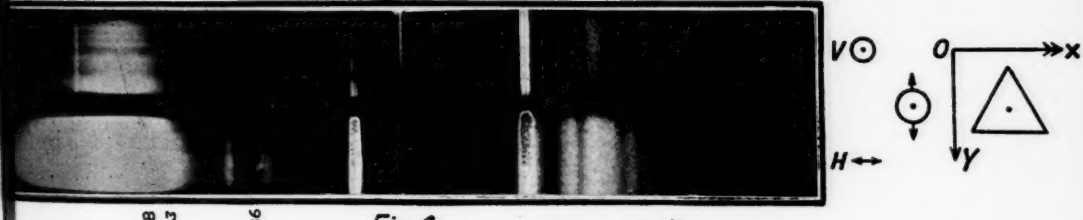


Fig.4

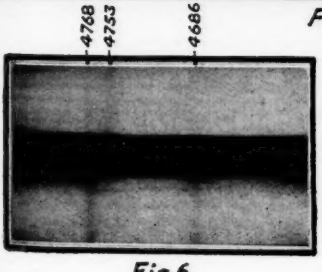


Fig.6

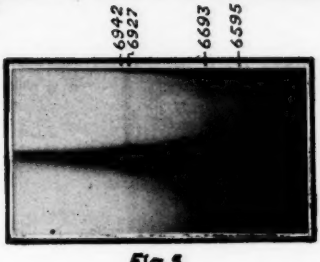
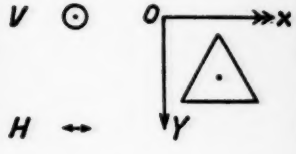


Fig.5



FIGS. 1-4. Fluorescence Spectra of Ruby

FIGS. 5-6. Absorption Spectra of Ruby

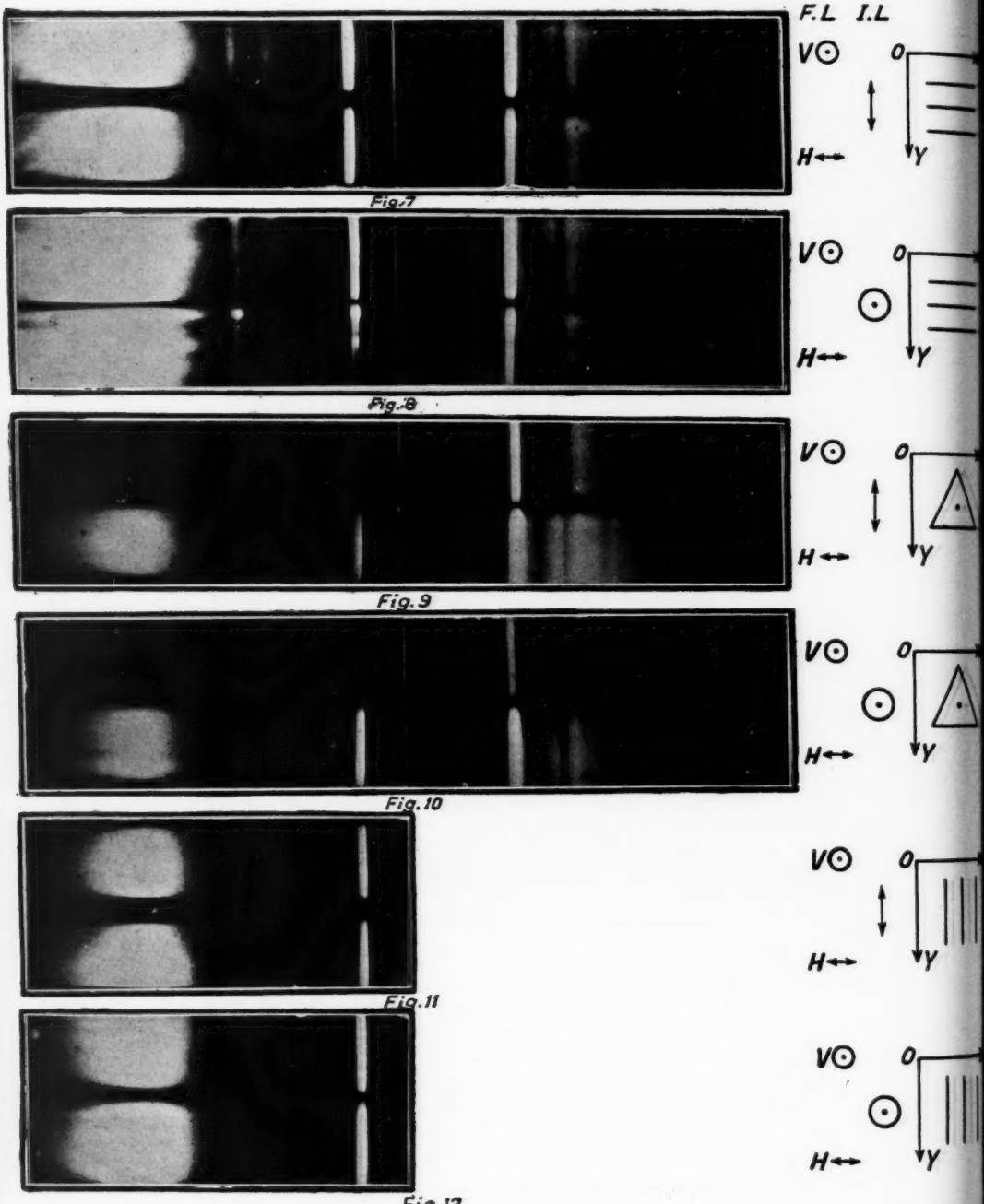


Fig.7

Fig.8

Fig.9

Fig.10

Fig.11

Fig.12

Fluorescence Spectra of Ruby